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UNITED STATES BUREAU OF MINES
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INFORMATION CIRCULAR

MANGANESE; ITS OCCURRENCE, MILLING, AND METALLURGY

PART II.

CHAPTER 5. THERMODYNAMIC PROPERTIES OF MANGANESE, AND ITS METALLURGICALLY IMPORTANT COMPOUNDS

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C. G. MAIER

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UNITED STATES BUREAU OF MINES

MANGANESE: ITS OCCURRENCE, MILLING, AND METALLURGY[1]

Part II

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CHAPTER 5. THERMODYNAMIC PROPERTIES OF MANGANESE, AND ITS METALLURGICALLY IMPORTANT COMPOUNDS

By C. G. Maier[2]

The present trend of chemicometallurgical research toward widespread and inclusive use of thermodynamic methods requires the inclusion of available data of this sort in any comprehensive metallurgical report. Such data for manganese are far from adequate for the full utilization of these methods. Even if our knowledge of these properties is weak, the collection of available figures is nevertheless well worth while, especially if their utilization in an approximate way may show inherent possibilities of application. No less important is the necessity for discovering the vital gaps in the existing information, to serve as a basis for further pertinent study.

The utility of the thermodynamic methods of Lewis and Randall (234)[3] has become increasingly evident to metallurgists. It is true that at present no better approach to the general, fundamental problems of chemical metallurgy is available than close adherence to these methods. The effort is here made to collect and correlate, as far as possible, significant quantitative thermodynamic data on manganese and its metallurgically important compounds. There are considered here only the intrinsic properties of pure materials. The order maintained as far as possible will be as follows:

1. Specific heats at low temperatures.
   (a) Compressibility, thermal expansiveness and atomic volume.
   (b) Entropy calculated from specific heats.
2. Specific heats at high temperatures.
3. Sublimation and vapor pressures.
4. Thermal data.
   (a) Heats involved in change of state; sublimation, fusion, vaporization, transitions.
   (b) Heats of formation of compounds.
   (c) Free energies of formation.
5. Correlation of heats, free energies, and entropies, where possible.

METALLIC MANGANESE

Allotropy

The question of the allotropy of manganese has already been discussed. There would seem to be little doubt as to the actual existence of at least three forms of manganese, but from a thermodynamic viewpoint interest is confined to transformations having definite and measurable energy quantities

2 Supervising Engineer, fundamental studies section, Metallurgical Division, U. S. Bureau of Mines.

3 Throughout parts I to IV, numbers in parentheses refer to items in this bibliography, and page numbers to those in the reference cited.

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associated with the change of form. Here recourse must be had to specific heat measurements at high temperatures. In a later section it will be shown that the available specific heat measurements indicate such energy changes at 835° and 1,044°C. only.

Comparison of these transition temperatures with those obtained by means other than specific heat measurements seems very unsatisfactory, but it must be remembered that such changes often show time and temperature lags, especially the latter when impure materials are considered. For the present purpose, therefore, it may suffice to accept the points derived from specific heats as valid, and the assumption will be made that up to 835°C the α form is stable, from 835 to 1,044° the β form exists, and above 1,044° the specific-heat methods really involved the tetragonal γ form.

Specific Heats at Low Temperatures

No measurements of true specific heat at low temperatures are reported. A few measurements of mean specific heat have been made by Dewar (70), by Estriecher and Staniewski (86), and by Nordmeyer and Bernulli (277). In a recent resume of low-temperature specific heat and entropy data, Kelley (200) has selected the data of Dewar as most suitable for entropy calculations, and reports $S_{298} = 7.3 \pm 0.5$.

Determination of the true specific heat of manganese metal at low temperatures is an assigned problem for investigation at the Pacific Experiment Station of the Bureau of Mines.

Compressibility, Expansion, and Atomic Volume

The only available determination of the compressibility of manganese is that of Richards (315), who reported $0.84 \cdot 10^{-6}$ per megabar and who also gave 7.7 for the atomic volume and 7.37 for the density at 20°C. Available figures for thermal expansiveness are those of Disch (71), who gives $1.59 \cdot 10^{-5}$ between -190 and 0°C., and $2.28 \cdot 10^{-5}$ between 0° and 100°C. The difference between the specific heats at constant pressure and volume may be calculated from the thermodynamic expression

$$C_p - C_v = \frac{9\alpha^2 v T}{\beta} \qquad \text{(Equation 1)}$$

where C_p and C_v are the respective specific heats at constant pressure and volume, α the linear expansion coefficient, v the specific volume, T the absolute temperature, and β the compression coefficient. At 25°C. substitution of the various figures given results in the value 0.3 calorie per degree for the specific heat difference.

A recent determination of the density of manganese (44) indicates a value of 7.76 for the gram-atomic volume compared with the older figure, 7.34. The corresponding densities are 7.08 and 7.48. It seems, however, that Campbell

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had for his density determinations electrolytic material of the γ or tetragonal form, and it is not strange that his results should be low.

According to Matsuyama (244), manganese contracts 1.7 percent of its volume during solidification. Assuming that the coefficient of expansion of the three forms of manganese can be considered equal for approximate calculation the densities and specific volumes may be summarized, as in table 41.

TABLE 41. - Densities and Specific Volume of Manganese

Form of Mn	Type measurement	Temperature, °C.	Density	Specific volume
α	Direct	20	7.37	7.45
α	X ray	20	7.44	7.38
α	Calc.	835	7.04	7.80
β	X ray	20	7.29	7.54
β	Calc.(X ray)	835	6.89	7.98
γ	Direct	20	7.08	7.76
γ	X ray	20	7.21	7.62
γ	Calc.(X ray)	1,044	6.73	8.16
γ	do	1,220	6.65	8.26
Liquid	Calc.	1,220	6.54	8.40

Specific Heats at High Temperatures

Available data on the specific heat of manganese at high temperatures consist of the measurements of Umino (373), of Wüst, Meuthen, and Durer, (401), of Stücker (363), and of Läemmel (226).

K. K. Kelley, of the Pacific Experiment Station of the Bureau of Mines, has recently made a critical study of high-temperature specific heats in connection with a bulletin on this subject now in preparation. He reports that the data of Umino are the best available, as determined by a comparative plot of total heats as determined by all these experimenters. Table 42 shows the total heats taken from Kelley's smoothed curve.

The reader will note that the melting point of manganese is taken at 1,220°C. Umino's figure was 1,221°C. Some nine other figures are given in the Landolt-Börnstein Tabellen (227), and Burgess (42) has reported a value obtained by a micromelting apparatus.

The mean of all values (11 in number) is 1,223° ± 13, but of these, two sets, including that of Burgess, are discordantly high.[4] When the two high values are omitted from the average it becomes 1,217° ± 8. This figure has

4 Several values in the Tabellen are based upon a comparison which involved taking the melting point of nickel at 1,484°C. These figures have been corrected in the average by the author to correspond to a melting point for nickel of 1452.3°C.

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been rounded off to 1,220° and has been used as more consistent with the thermodynamic data available than the higher figure of Gayler (108) given in chapter 1.

TABLE 42. - Total Heats for Manganese Metal from 0°C., Calories per Gram-Atom

Form of Mn	Temperature, °C.	Heat content (curve)	Difference, curve-Umino, percent
α	0	0	0
	50	299	---
	100	617	1.3
	150	953	---
	200	1,308	.5
	250	1,681	---
	300	2,072	1.0
	350	2,482	.7
	400	2,911	1.3
	450	3,358	.2
	500	3,823	-.2
	550	4,307	-.4
	600	4,809	-.2
	650	5,330	-.5
	700	5,869	-.3
	750	6,427	---
	800	7,003	---
	835	7,417	---
α-β	835	148	-6.0
β	835	7,565	---
	850	7,700	0.9
	900	8,150	.2
	950	8,600	-1.1
	1,000	9,050	-.9
	1,044	9,446	---
β-γ	1,044	244	-2.0
γ	1,044	9,690	---
	1,050	9,750	+.1
	1,100	10,250	---
	1,150	10,750	-1.0
	1,200	11,250	-1.0
	1,220	11,450	---
γ-liquid.....	1,220	3,576	+.5
Liquid.....	1,220	15,026	---
	1,250	15,365	-.1
	1,300	15,930	+.4
	1,350	16,495	+.1
	1,400	17,060	-.1

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For many purposes the figures in table 42 may be found more convenient than analytical expressions for specific heat, since some complications due to allotropy may be avoided in certain cases by the summation of total heats. Kelley has derived certain analytic expressions for heat content of the various forms, which are summarized in table 43.

TABLE 43. - Heat Content of Manganese From 0° C.
(Formula, $H_c = a + bt + ct^2$---)

Form of Mn	a	b	c	Temperature range, °C.
α	0	5.80	$3.692 \cdot 10^{-3}$	0 - 835
β	50.0	9.00	---	835 - 1,044
γ	-750	10.00	---	1,044-1,220
Liquid	1,240	11.30	---	1,220-1,400

By differentiation of these expressions and substitution of $T = t + 273.1$, the following equations are derivable for true specific heat.

$$C_p(\alpha\ \text{Mn}) = 3.78 + 7.38 \cdot 10^{-3} T,$$
$$C_p(\beta\ \text{Mn}) = 9.00,$$
$$C_p(\gamma\ \text{Mn}) = 10.00,$$
$$C_p(\text{liq.}) = 11.30.$$

Sublimation and Vapor Pressures

Actual measurements of vapor pressures of manganese metal are meager. Greenwood (122, 123) reported a boiling point of 1,900°C. Observed temperatures varied about 100°; mean values were stated to be concordant to 20°. The melt was contained in a carbon crucible with MgO lining. In this connection, Tiede and Birnbräuer (372) have shown that manganese readily reduced MgO at higher temperatures. This would justify the assumption that the observed boiling point of Greenwood was too low.

Ruff and Bormann (328) determined the boiling point at 30 mm pressure for pure metal to be 1,511°C. Millar (258) has calculated vapor pressures for manganese, using Greenwood's boiling point combined with Wüst's specific-heat data.

In a recent article by Gayler (109) pure manganese is said to volatilize under 1 to 2 mm pressure at a temperature just above the melting point (1,225°C).

It seems highly probable that the measurements of Ruff and Bormann are the best available. If the assumption is made that these latter figures are approximately correct, a much more satisfactory calculation of the vapor pressure of manganese becomes possible, especially since the energy of the gas may be determined from spectroscopic data. Through the courtesy of Prof. W. F. Giauque (111) it is possible to include here recent results of such a calculation from spectroscopic data, the specific results being given in table 44.

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TABLE 44. - Free Energy of Manganese Vapor from Spectroscopic Data

T, °K.	$-\frac{F^\circ - E_o^\circ}{T}$	T, °K.	$-\frac{F^\circ - E_o^\circ}{T}$
298.1	36.534	1,700	45.182
500	39.103	1,900	45.734
700	40.774	2,100	46.231
900	42.022	2,300	46.683
1,100	43.019	2,500	47.098
1,300	43.849	2,700	47.481
1,500	44.560	2,900	47.838

The symbol F° in table 44 refers to the free energy of the vapor in the standard state, and E_o° is the energy in the standard state at absolute zero. For further discussion of the methods used in obtaining these figures and explanation of the symbols the reader is referred to the article by Professor Giauque (110).

To use these figures for calculation of vapor pressures similar information is necessary with respect to the solid and liquid. Thus, assuming the solid to be the standard state, equation (30) in Giauque's paper above may be used:

$$F^\circ - E_o^\circ = \int_o^T C_p dt - T \int_o^T C_p d \ln T . \quad \text{(Equation 2)}$$

The first integral is obviously the total heat from 0°K. and the second the entropy. For the present purpose the specific heats for the various forms of manganese may be integrated more conveniently from 0°C. or from 298.1°K. in the case of total heat and of entropy, respectively, with the addition of appropriate corrections from low-temperature data to carry the results to absolute zero. Thus, in the case of entropy the addition involved here amounts to 7.3 units, as given previously (see p. 100). Similarly, by drawing a Debye curve through and below Dewar's low-temperature data for manganese and extending it upward to meet the herein accepted value for the specific heat at 0°C., as previously given, the total heat of manganese up to 273.1° K. may be obtained as 1,000 ± 50 calories. The total heats at various upper temperatures are then given by the addition of 1,000 calories to the figures of table 42, and the corresponding entropies are calculated from the formulas given for specific heat, with suitable corrections for the transitions involved.

The results of such a series of calculations are given in table 45.

To calculate vapor pressures, consider the equilibrium $Mn_{(l)} = Mn_{(g)}$ at 1,511°C. or 1,784°K., where, according to Ruff and Bormann, the vapor pressure is 30 mm.

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Then, $\Delta F^{\circ}_{1,784} = -R\ T\ \ln \frac{30}{760}$,

$$\frac{\Delta F^{\circ}}{T} = -R \cdot 2.3026 \log \frac{30}{760} ,$$

$$= 6.43 .$$

Now for the reaction, by interpolation in tables 44 and 45, for $T = 1,784$,

$$-\frac{(F^{\circ}-E^{\circ}_{o})}{T}_{(gas)} - \frac{(F^{\circ}-E^{\circ}_{o})}{T}_{(l)} = -\frac{\Delta F^{\circ}}{T} + \frac{\Delta E^{\circ}_{o}}{T} ,$$

$$45.42 - 15.50 = -6.43 + \frac{\Delta E^{\circ}_{o}}{T} ,$$

$$\left(\frac{\Delta E^{\circ}_{o}}{T}\right)_{1,784} = 36.35.$$

From this last result, corresponding figures for $\frac{\Delta E^{\circ}_{o}}{T}$ at any desired temperatures are calculated directly and combined with the values of $\frac{F^{\circ}-E^{\circ}_{o}}{T}$ for solid, liquid, and gas to furnish directly the free energy of vaporization. Such calculated results are shown in table 46. Since $\frac{\Delta F^{\circ}}{T} = -R \ln p$, the corresponding vapor pressures are readily calculated and are shown in various forms in the last three columns of the table. For purposes of interpolation a curve showing the variation of log V.P. v. $T^{\circ}C$. is reproduced in figure 8.

TABLE 45. - Free Energy of Solid and Liquid Manganese

Form of Mn	Temperature °C.	Temperature °K.	H	$\frac{H}{T}$	S	$-\frac{F^{\circ}-E^{\circ}_{o}}{T}$
α.....	25	298.1	1,146	3.84	7.3	3.46
	835	1,108	8,417	7.59	18.43	10.84
β.....	835	1,108	8,565	7.72	18.56	10.84
	900	1,173	9,150	7.80	19.07	11.27
	1,000	1,273	10,050	7.86	19.82	11.96
	1,044	1,317	10,446	7.92	20.49	12.57
γ.....	1,044	1,317	10,690	8.11	20.68	12.57
	1,100	1,373	11,250	8.19	21.08	12.89
	1,200	1,473	12,250	8.31	21.86	13.55
	1,220	1,493	12,450	8.34	21.92	13.58
Liquid....	1,220	1,493	16,026	10.73	24.31	13.58
	1,300	1,573	16,930	10.76	24.90	14.14
	1,400	1,673	18,060	10.80	25.60	14.80
	1,500	1,773	19,190	10.82	26.26	15.44
	1,600	1,873	20,320	10.85	26.88	16.03
	1,700	1,973	21,450	10.87	27.46	16.59
	1,800	2,073	22,580	10.89	28.02	17.13
	1,900	2,173	23,710	10.91	28.56	17.65
	2,000	2,273	24,840	10,93	29.07	18.14

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In comparing the calculated vapor pressures in table 46 with the available direct determinations the reader will note that the boiling point is 2,000°C. compared to Greenwood's 1,900°, the difference being just that given by Greenwood himself as the reproducibility of his results. Furthermore, at the melting point the figure 1.46 mm is calculated, where the previously mentioned data of Gayler indicate a vapor pressure of 1 to 2 mm, an almost exact concordance but considerably different from Millar's calculated figures. The vapor pressure at 1,250°C., corresponding to Gayler's melting point, would be just a little over 2 mm.

Although application of the calculation of energy from spectroscopic data to vapor pressures still involves the supposition of monatomic gas in this case the figures so obtained are undoubtedly far superior to the usual calculation from the Sackur equation, which was essentially the basis of Millar's method. Should a better boiling-point or vapor-pressure measurement than that of Ruff and Bormann become available, recalculation from the original figures of table 44 would leave little to be desired, since the errors in the calculation must come almost entirely from the fixed point taken and from the free-energy figures for solid and liquid. Even with these limitations in mind the results must be regarded as highly satisfactory.

TABLE 46. - Calculated Vapor Pressures of Manganese Metal

Form of Mn	Temperature °C.	Temperature °K.	$-\frac{F^\circ-E_o^\circ}{T}$ Gas	$-\frac{F^\circ-E_o^\circ}{T}$ Solid or liquid	$\frac{\Delta E_o^\circ}{T}$ (s)-(g) or (l)-(g)	$\frac{\Delta F^\circ}{T}$	Log V.P.	V.P. Atmospheres	V.P. Millimeters
α....	25	298.1	36.53	3.46	217.25	184.18	-40.22	$6\cdot10^{-41}$	
	835	1,108	43.05	10.84	58.48	26.27	--5.740	$1.82\cdot10^{-6}$	$1.3\cdot10^{-3}$
β....	835	1,108	43.05	10.84	58.48	26.27	-5.740	$1.82\cdot10^{-6}$	$1.3\cdot10^{-3}$
	900	1,173	43.33	11.27	55.25	23.19	-5.063	$8.65\cdot10^{-6}$	$6.58\cdot10^{-2}$
	1,000	1,273	43.74	11.96	50.90	19.12	-4.178	$6.64\cdot10^{-5}$	$5.05\cdot10^{-2}$
	1,044	1,317	43.91	12.57	49.20	17.86	-3.903	$1.25\cdot10^{-4}$	.0950
γ....	1,044	1,317	43.91	12.57	49.20	17.86	-3.903	$1.25\cdot10^{-4}$	.0950
	1,100	1,373	44.12	12.89	47.20	15.97	-3.490	$3.24\cdot10^{-4}$	.246
	1,200	1,473	44.47	13.55	44.00	13.08	-2.857	$1.39\cdot10^{-3}$	1.06
	1,220	1,493	44.54	13.58	43.41	12.45	-2.720	$1.915\cdot10^{-3}$	1.455
Liquid	1,220	1,493	44.54	13.58	43.41	12.45	-2.720	$1.915\cdot10^{-3}$	1.455
	1,300	1,573	44.79	14.14	41.21	10.56	-2.308	$4.92\cdot10^{-3}$	3.74
	1,400	1,673	45.10	14.80	38.74	8.44	-1.844	$1.43\cdot10^{-2}$	10.9
	1,500	1,773	45.39	15.44	36.58	6.63	-1.448	$3.57\cdot10^{-2}$	28.7
	1,600	1,873	45.66	16.03	34.61	4.98	-1.088	$8.17\cdot10^{-2}$	62.1
	1,700	1,973	45.92	16.59	32.87	3.54	-.773	$1.69\cdot10^{-1}$	128.5
	1,800	2,073	46.17	17.13	31.26	2.22	-.485	$3.27\cdot10^{-1}$	249.
	1,900	2,173	46.40	17.65	29.81	1.06	-.232	$5.86\cdot10^{-1}$	446.
	2,000	2,273	46.62	18.14	28.50	.02	-.004	$9.99\cdot10^{-1}$	760.

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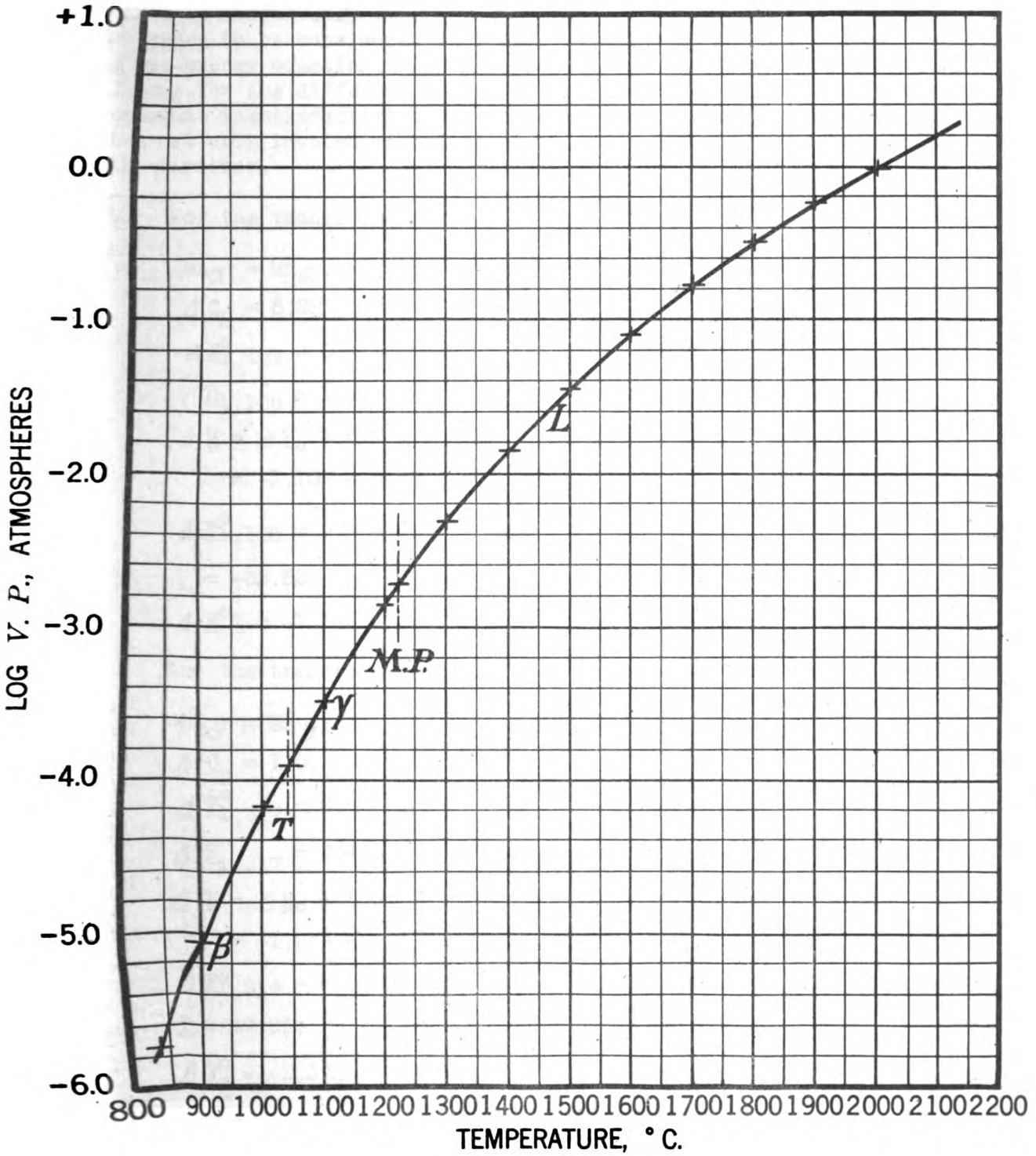

Figure 8.- Vapor pressure of manganese metal; L, Liquid; γ, γ form, β, β form; M.P., melting point; T, transition.

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Thermal Data

Although the tabular method of calculating free energies used for vapor pressures is undoubtedly superior when the necessary data are available, most of the cases to be considered will be dealt with in the analytical form of standard free-energy equation. One may proceed to write such equations in a purely formal way for the different states of manganese, bearing in mind that despite the somewhat unsatisfactory nature of some of the specific-heat data, most cases if interest will involve cancellation (either implicit or explicit) of the uncertain portions.

1. For the transformation,

$$Mn_{\alpha} = Mn_{\beta},$$

$$\Delta \underline{C}_p = 5.22 - 7.38 \cdot 10^{-3} \underline{T},$$

$$\Delta \underline{F}^{\circ}_{1,108} = 0,$$

$$\Delta \underline{H}_{1,108} = 148,$$

$$\Delta \underline{H} = \Delta \underline{H}_o + 522\ \underline{T} - 3.69 \cdot 10^{-3} \underline{T}^2,$$

$$= -1,102 + 5.22\ \underline{T} - 3.69 \cdot 10^{-3} \underline{T}^2. \qquad \text{(Equation 3)}$$

$$\Delta \underline{F}^{\circ}_{1,108} = 0 = -1,102 - 5.22\ \underline{T}\ \underline{\ln}\ \underline{T} + 3.69 \cdot 10^{-3} \underline{T}^2 + \underline{I}\ \underline{T},$$

$$\underline{I} = +33.52,$$

$$\Delta \underline{F}^{\circ}\underline{T} = -1,102 - 5.22\ \underline{T}\ \underline{\ln}\ \underline{T} + 3.69 \cdot 10^{-3} \underline{T}^2 + 33.52\ \underline{T}. \qquad \text{(Equation 4)}$$

2. For the transformation,

$$Mn_{\beta} = Mn_{\gamma},$$

$$\Delta \underline{C}_p = 1.0,$$

$$\Delta \underline{F}^{\circ}_{1,317} = 0,$$

$$\Delta \underline{H}_{1,317} = 244,$$

$$\Delta \underline{H} = \Delta \underline{H}_o + 1.0\ \underline{T},$$

$$= -1,073 + 1.0\ \underline{T}. \qquad \text{(Equation 5)}$$

$$\Delta \underline{F}^{\circ}_{1,317} = -1,073 - 1.0\ \underline{T}\ \underline{\ln}\ \underline{T} + \underline{I}\ \underline{T},$$

$$\underline{I} = +7.99,$$

$$\Delta \underline{F}^{\circ}_{\underline{T}} = -1,073 - 1.0\ \underline{T}\ \underline{\ln}\ \underline{T} + 7.99\ \underline{T}. \qquad \text{(Equation 6)}$$

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3. For the transformation,

$$Mn_{\gamma} = Mn_{(l)},$$

$$\Delta \underline{C_p} = 1.30,$$

$$\Delta \underline{F}^{\circ}_{1,493} = 0,$$

$$\Delta \underline{H}_{1,493} = 3,576,$$

$$\Delta \underline{H} = \Delta H_0 + 1.30\ \underline{T},$$

$$= -5,516 + 1.30\ \underline{T}. \qquad \text{(Equation 7)}$$

$$\Delta \underline{F}^{\circ}_{1,493} = 0 = -5,516 - 1.30\ \underline{T}\ \underline{\ln}\ \underline{T} + \underline{I}\ \underline{T},$$

$$\underline{I} = +11.01,$$

$$\Delta \underline{F}^{\circ}_{\underline{T}} = -5,516 - 1.30\ \underline{T}\ \underline{\ln}\ \underline{T} + 11.01\ \underline{T}. \qquad \text{(Equation 8)}$$

4. For the transformation,

$$Mn_{(l)} = Mn_{(g)},$$

$$\Delta \underline{C_p} = -6.33,$$

$$\Delta \underline{F}^{\circ}_{1,784} = -\underline{RT}\ \underline{\ln}\ \frac{30}{760} = +11,460,$$

$$\Delta \underline{F}^{\circ}_{2,274} = 0 \text{ (normal boiling point)},$$

$$\Delta \underline{F}^{\circ}_{1,784} = +11,460 = \Delta \underline{H}_0 + 6.33\ \underline{T}\ \underline{\ln}\ \underline{T} + \underline{I}\ \underline{T},$$

$$\Delta \underline{F}^{\circ}_{2,274} = 0 = \Delta \underline{H}_0 + 6.33\ \underline{T}\ \underline{\ln}\ \underline{T} + \underline{I}\ \underline{T}.$$

Solving simultaneously,

$$\underline{I} = -77.92,$$

$$\Delta \underline{H}_0 = +65,930,$$

$$\Delta \underline{F}^{\circ}_{\underline{T}} = +65,930 + 6.33\ \underline{T}\ \underline{\ln}\ \underline{T} - 77.92\ \underline{T}. \qquad \text{(Equation 9)}$$

$$\Delta \underline{H} = +65,930 - 6.33\ \underline{T}. \qquad \text{(Equation 10)}$$

5. By adding equations 3 and 5, and 4 and 6, for the transformation,

$$Mn_{\alpha} = Mn_{\gamma},$$

$$\Delta \underline{H} = -2,175 + 6.22\ \underline{T} - 3.69 \cdot 10^{-3} \underline{T}^2. \qquad \text{(Equation 11)}$$

$$\Delta \underline{F}^{\circ}_{\underline{T}} = -2,175 - 6.22\ \underline{T}\ \underline{\ln}\ \underline{T} + 3.69 \cdot 10^{-3} \underline{T}^2 + 41.46\ \underline{T}. \qquad \text{(Equation 12)}$$

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Similarly, from equations 7 and 11, and 8 and 12, for the transformation,

$$Mn_{(\alpha)} = Mn_{(l)}$$

$$\Delta \underline{H} = -7,691 + 7.55\ \underline{T} - 3.69 \cdot 10^{-3} \underline{T}^2. \qquad \text{(Equation 13)}$$

$$\Delta \underline{F}^{\circ}_{\underline{T}} = -7,691 - 7.55\ \underline{T}\ \underline{\ln}\ \underline{T} + 3.69 \cdot 10^{-3} \underline{T}^2 + 52.47\ \underline{T}. \qquad \text{(Equation 14)}$$

Finally, by the addition of equations 13 and 10, and 14 and 9, for the transformation,

$$Mn_{(\alpha)} = Mn_{(g)},$$

$$\Delta \underline{H} = +58,239 + 1.22\ \underline{T} - 3.69 \cdot 10^{-3} \underline{T}^2. \qquad \text{(Equation 15)}$$

$$\Delta \underline{F}^{\circ}_{\underline{T}} = +58,239 - 1.22\ \underline{T}\ \underline{\ln}\ \underline{T} + 3.69 \cdot 10^{-3} \underline{T}^2 - 25.45\ \underline{T}. \qquad \text{(Equation 16)}$$

These last equations will be useful in referring reactions involving manganese vapor to the standard state of solid α Mn.

Manganese Ion

The free energy of the manganese ion is a quantity that may be used in calculating the free energy of formation from solubility measurements. Because early experiments on the electrode potential of manganese were unsatisfactory, Lewis and Randall did not include the manganous ion in their resume of standard electrode potentials.

The manganese electrode is very sensitive to oxygen when used in electrolytic cells, and the ordinary form of cast metal shows erratic behavior. Royce and Kahlenberg (321) have, however, obtained consistent behavior, using especial precautions to avoid the presence of oxygen in these cells, and experimenting with various concentrations of manganese amalgam. Their results indicate that amalgams above 1 percent show substantially constant electro motive force in a given concentration of electrolyte. Table 47 shows selected portions of these results and various calculations which have been made from them.

TABLE 47. - Electrode Potential of Manganese at 20°C.

Electrolyte	Stated normality	m, molality	e.m.f. reported	Cell e.m.f.	e.m.f. v. H_2	γ activity coefficient	Correction	E° standard electrode potential
$MnSO_4$	1.0	0.5	1.4490	0.8890	1.1712	0.110	0.0366	1.1346
do.	.5	.25	1.4530	.8930	1.1752	.157	.0409	1.1343
$MnCl_2$	1.0	.5	1.4335	.8735	1.1557	.490	.0178	1.1379
do.	.5	.25	1.4380	.8780	1.1602	.498	.0263	1.1339
Average	----	----	----	----	----	----	----	1.1352 ±0.0011

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In this table the figures given by the authors for "normality" seem in fact to be double molalities rather than equivalents per liter solution. Nowhere in their article do the authors state specifically what they mean by "normality", but a clue is furnished by the statement they make that "8-normal" solution is virtually saturated at ordinary temperatures. A saturated solution contains approximately 39 percent $MnSO_4$, formula weight 151, density of solution about 1.4. Thus a truly 8-normal solution would contain $\frac{8 \times 75.5}{1,400} = 43$ percent $MnSO_4$, but a 4-molal solution contains $\frac{8 \times 75.5}{8 \times 75.5 + 1,000} = 37.8$ percent $MnSO_4$.

The electro motive force reported by the authors is stated to be based on the value +0.560 volt for the normal calomel electrode used as reference standard. To put these results on the basis of the hydrogen electrode, as used by Lewis and Randall (234, p.407), we shall subtract 0.560 and add 0.2822, the latter figure being the electro motive force of the normal electrode selected by these authors. In this way the figures given in the column headed "e.m.f. v. H_2" are obtained. The activity coefficients in the next column are taken from Landolt-Börnstein (228). Then, since $E = E_0 - \frac{RT}{2F} \ln (\gamma m)$, the correction term represented by the last quantity of this formula may be calculated and the standard electrode potential E_0 found directly.

Inspection of the values of E_0 so obtained shows good consistency between the various measurements. Accepting the average result given, there is obtained for the reaction $Mn(Hg) \longrightarrow Mn^{++}$,

$$\Delta F^{o}_{291} = -NFE_0 = -2 \times 23,074 \times 1.1352,$$

$$= -52,450 \text{ calories.}$$

Although the indicated deviation from the mean of the above value for E_0 would show an apparent deviation from the mean of 50 calories in free energy, it must not be forgotten that the cells used by Royce and Kahlenberg may have contained liquid-junction potentials of unknown amount that could in extreme cases represent 500 calories or more.

OXIDES OF MANGANESE

Manganous Oxide

This material occurs in nature as the mineral manganosite and so far as is known does not show allotropism. The density of the natural mineral is approximately 5.1.

Specific Heats at Low Temperatures

The only available information regarding low-temperature specific heats of manganous oxide are the measurements by Millar (257). In his review of low-temperature specific heats, Kelley (200) has corrected Millar's original data slightly and reports $S_{298.1} = 14.4 \pm 0.6$. Millar had calculated $S_{298} = 14.92$.

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Kelley's value will be accepted here. Data on compressibility and coefficient of expansion have not been found.

Specific Heats at High Temperatures

Previous to Millar's low-temperature work the only reported specific heat of manganous oxide was that of Regnault (312), who reported a mean value of 11.14 between 13° and 98°C. The true specific heat from Millar's experiments at 0°C. is 10.00, indicating that Regnault's result is too high.

In the absence of data on the specific heat at high temperatures the only estimate possible is a rational guess based on the figure at 0°C. Then it may be assumed that at the melting point of MnO, which has been given by Tiede and Birnbräuer (372) as 1,650°C., a maximum true specific heat of 14 calories per formula weight[5] has been reached.

Consider now the conventional quadratic expression used by Lewis and Randall and others to represent specific heats at high temperatures

$$C_p = a + bt + ct^2,$$

where a, b, and c are numerical coefficients and t the temperature in degrees centigrade. Coefficient a is obviously the value at $t = 0$, that is, for MnO = 10.00. If the quadratic is differentiated

$$\frac{dC_p}{dt} = b + 2ct,$$

$$\left(\frac{dC_p}{dt}\right)_{t = 0} = b,$$

then b is the slope of the specific-heat curve at $T = 273.1$, and c is determined by the limiting value of $C_p = 14$ at 1,650°C.

From Millar's specific-heat curve, $b = 8.4 \cdot 10^{-3}$ is found, and $c = -3.62 \cdot 10^{-6}$ from which

$$C_p(MnO) = 10.00 + 8.4 \cdot 10^{-3} t - 3.62 \cdot 10^{-6} t^2.$$

Substituting $t = T - 273.1$,

$$C_p(MnO) = 7.43 + 1.038 \cdot 10^{-2} T - 3.62 \cdot 10^{-6} T^2. \qquad \text{(Equation 17)}$$

---

5 The figure 14 is crudely estimated as follows: C_v for Mn and O may approach the theoretic value of 6 calories each. At high temperatures the specific heats of the compound will be nearly additively the sum of the specific heats of its constituent elements. $C_p - C_v$ is 0.3 at 298.1°K, and because of the hardness of manganese, may be expected to increase fairly rapidly with the temperature. Actual values of C_p tend to drift somewhat higher than 6 calories per gram atom. $(C_p - C_v)$, by analogy with zinc oxide, which has about the same stability as MnO and a formula weight of the same order of magnitude the figure 13.9 is estimated for ZnO near its sublimation point (1,900°C.). Mean specific heat 25° to 1,100°C. (W.P.White), 12.16; true specific heat at 25°C. 9.75. $\frac{19}{11}$ x (12.16 - 9.75) + 9.75 = 13.9.

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Sublimation and Vapor Pressures

In spite of the fact that Berthelot (24) and Le Chatelier (230) are in substantial agreement with 90,900 and 90,800 calories for the heat of formation of manganous oxide, the figure selected here is the recent one of Roth (319), who reports 96,500 ± 650 calories for the heat of formation at constant pressure.

Then for the reaction

$$Mn(\alpha) + \tfrac{1}{2}O_2 = MnO,$$

$$S_{298} = 7.5 \quad + 24.5 - 14.4 \qquad \Delta S_{298} = 17.4,$$

$$\Delta h_{298} = -96,500,$$

$$\Delta F_{298} = \Delta H - T\Delta S,$$

$$= -91,310,$$

$$\Delta C_p = 0.40 + 2.50\cdot10^{-3}T - 3.62\cdot10^{-6}T^2,$$

$$-96,500 = \Delta H = \Delta H_0 + 0.4\ T + 1.25\cdot10^{-3}T^2 - 1.21\cdot10^{-6}T^3,$$

$$\Delta H_0 = -96,700,$$

$$-91,310 = \Delta F^0_{298} = -96,700 - 0.4\ T\ \ln T - 1.25\cdot10^{-3}T^2 + 0.60\cdot10^{-6}T^3 + I\ T,$$

$$I = +20.68,$$

$$\Delta F^0_T = -96,700 - 0.4\ T\ \ln T - 1.25\cdot10^{-3}T^2 + 0.60\cdot10^{-6}T^3 + 20.68\ T.$$

(Equation 19)

Free Energy of MnO and $Mn(OH)_2$ from Solubility

The free energy of the Mn^{++} ion obtained in a previous section of this chapter may be used to calculate an approximate value for the free energy of $Mn(OH)_2$, using the solubility measurements of Sackur and Fritzmann (332) for this last material. These authors report a solubility of 2.15 moles per liter determined from a conductivity of $1.39\cdot10^{-5}$ for the saturated solution in the presence of barium sulphate, and of conductivity water $2.\cdot10^{-6}$. They measured the conductivity when successive portions of approximately 1/100-normal $Ba(OH)_2$ solution were added to 1/100-normal $MnSO_4$, taking the minimum value so obtained as the lowest observable point. Upon replotting the original data and drawing straight lines through the points nearest the minimum, as seems justified by the data, the figure $1.05\cdot10^{-5}$ is obtained for the minimum conductivity. Correcting for the $BaSO_4$ and conductivity water, the new figure is $6.2\cdot10^{-6}$ for the conductivity due to $Mn(OH)_2$. Taking 174 for the ion mobility of the OH^- ion and 44 for $\frac{1}{2}\ Mn^{++}$, the normal concentration (c) of $Mn(OH)_2$ is

$$c = \frac{1,000\cdot6.2\cdot10^{-6}}{218} = 2.84\cdot10^{-5},$$

and the molal solubility is $1.42\cdot10^{-5}$.

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Then for the reaction

$$Mn(OH)_2 = Mn^{++} + 2OH^-,$$

the free energy of the reaction is

$$\Delta \underline{F}^{\circ}_{291} = \underline{RT}\ \underline{\ln}\ (\underline{a}_{Mn^{++}}) \cdot (\underline{a}_{OH^-})^2,$$

where (Mn^{++}) is $1.42 \cdot 10^{-5}$, and (OH^-) is $2.84 \cdot 10^{-5}$, if it is assumed that the activity coefficient in these very dilute solutions is unity. The numerical result is $\Delta \underline{F}^{\circ}_{291} = +18,600$. Lewis and Randall give for the free energy of the hydroxide ion -37,455 calories, from which, by summation in accordance with the above reaction, $\Delta \underline{F}^{\circ}_{291}\ Mn(OH)_2 = -145,960$ calories. It is difficult to estimate the accuracy of this latter figure, but it must be compared to the value -91,310 for MnO, obtained from the third-law calculation.

To make such comparison, an estimate of the entropy of $Mn(OH)_2$ and of the heat of hydration may be made. For the first item, it may be noted that the entropy of CaO is 9.5, and for $Ca(OH)_2$, 17.4, an increase of 8.0 units due to the water. Since $Mn(OH)_2$ is a much less stable hydroxide than $Ca(OH)_2$, it must necessarily be true that the entropy increase will be greater for the former than the latter. On the other hand, the difference cannot be as great as the entropy of ice, which may be taken as 11 units. The estimate may then be set at an increase of 9.5 over the oxide. Since MnO has an entropy of 14.4, the entropy of $Mn(OH)_2$ is estimated as 23.9 ± 1.5.

The heat of hydration of MnO must be small and may be zero. Mixter's (261) value of a heat evolution of 4,000 calories cannot be of great accuracy, because the peroxide method has been shown unreliable, but a low value is indicated.

Then for the reaction

$$MnO + H_2O = Mn(OH)_2,$$

$$\underline{S}_{298}\quad 14.4\quad 15.9\quad 23.9,$$

$$\Delta \underline{S} = -6.4,$$

$$\Delta \underline{H} = 0,$$

$$\Delta \underline{F}_{291} = \Delta H - \underline{T}\Delta \underline{S},$$

$$= +1,860.$$

If the value of free energy of liquid water is taken as -56,560 and for $Mn(OH)_2$ - 145,960, and these values are substituted in appropriate places for the above reaction, the free energy of MnO is calculated at 291°K. as -91,260. In the calculation the difference between entropies at 298° and 291°K. have been ignored in several places, and it is to be regarded as an approximation only.

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The concordance is more than could be expected in view of the devious methods used to obtain the two results. It must not be forgotten that the low-temperature specific heats of MnO show a marked anomaly, which makes the entropy calculation uncertain by 200 calories, and Roth's heat of formation is not claimed by him to be closer than 700 calories. These deviations alone might account for differences of several entropy units. Solubility measurements by conductivity are generally high, because of the possibility of unprecipitated impurities in the reagents used. Moreover, the measurements were made at different temperatures, and specific-heat data are lacking to reduce them to a common basis.

Higher Oxides of Manganese

Specific Heats

Manganic Oxide. - The mineral braunite is an impure manganic oxide, crystallizing in the tetragonal system and with a density of approximately 4.8. Thermodynamic data are meager. The only available specific heat is that of Ceberg (280), who gave 0.1620 for the mean specific heat per gram between 15° and 99°C. This may be taken as equivalent to 25.40 per formula weight at 57°C. In this case there are no data for direct determination of the b coefficient, and the best that can be done is to estimate it by analogy with Fe_2O_3. Parks and Kelley (291) have made measurements at low temperatures and find a true specific heat of Fe_2O_3 at 0°C. = 23.45. From the high-temperature specific heats of Roth and Bertram (320) one may estimate C_p (Fe_2O_3 at 47.5°C.) = 25.25. Then b is very nearly $\frac{25.25 - 23.45}{4.75} = 0.0390$.

Furthermore, it will be shown in a succeeding part of this work that b for MnO_2 is $3.09 \cdot 10^{-2}$ and from the MnO curve, b is $0.84 \cdot 10^{-2}$, so that if Mn_2O_3 is considered equal to $MnO + MnO_2$, b from this source should be $3.93 \cdot 10^{-2}$. Finally, a similar assumption as to the limiting value of C_p, as in the case of MnO, supposes in this case $C_p(Mn_2O_3) = 35$ at the temperature of dissociation of this material, which may be taken as 1,100°C. Then

$$a + 3.9 \cdot 10^{-2} t_1 + c t_1^2 = 25.40 \quad (t_1 = 57.0),$$

$$a + 3.9 \cdot 10^{-2} t_1 + c t_2^2 = 35.00 \quad (t_2 = 1{,}100),$$

whence $a = 23.26$, $c = -2.57 \cdot 10^{-5}$,

$$C_p(Mn_2O_3) = 23.26 + 3.9 \cdot 10^{-2} t - 2.57 \cdot 10^{-5} t^2,$$

$$\text{or } C_p(Mn_2O_3) = 10.33 + 5.3 \cdot 10^{-2} T - 2.57 \cdot 10^{-5} T^2. \qquad \text{(Equation 19)}$$

Mangano-Manganic Oxide. - The compound Mn_3O_4 exists in nature as the tetragonal crystals of hausmanite and has an approximate density of 4.8. Low-temperature specific heats have been determined by Millar, who reports $S_{298} = 35.73$. Kelley's recalculation of Millar's results is 35.5 ± 0.7, and this latter figure will be used in future calculations.

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The high temperature specific heats may be roughly estimated in the same manner as previously used for MnO. Thus $\underline{a} = \underline{C}_p 273.1 = 32.40$ from a curve of Millar's data, and from the slope of the curve at the same point $\underline{b} = 4.24 \cdot 10^{-2}$. No data as to the melting point are available, but it cannot be far from 1,500°C., at which temperature it may be assumed that the specific heat has reached a limiting value of 49 calories. Then

$$32.40 + 4.24 \cdot 10^{-2} \underline{t} + \underline{c}\underline{t}^2 = 49 \quad (\underline{t} = 1{,}500),$$

$$\underline{c} = -1.82 \cdot 10^{-5},$$

$$\underline{C}_p(Mn_3O_4) = 32.40 + 4.24 \cdot 10^{-2} \underline{t} - 2.09 \cdot 10^{-5} \underline{t}^2,$$

$$\text{or} \quad \underline{C}_p(Mn_3O_4) = 19.25 + 5.38 \cdot 10^{-2} \underline{T} - 2.09 \cdot 10^{-5} \underline{T}^2. \qquad \text{(Equation 20)}$$

Manganese Dioxide. - The compound MnO_2 is found in nature as rhombic crystals of pyrolusite, or tetragonal crystals of polianite, density about 4.8. Low-temperature measurements have been made by Russell, (331), who determined a few mean specific heats and more completely by Millar, whose data will be used here. A single mean specific heat from 17° to 48°C. is also reported by Kopp (210), whose result (13.8) virtually coincides with a slight extrapolation of Millar's points.

The entropy from Millar's data is $\underline{S}_{298} = 13.9 \pm 0.4$, the true specific heat at 0°C. 13.00, and $\left(\frac{d\underline{C}_p}{d\underline{t}}\right)_{\underline{t}=0} = \underline{b} = 3.09 \cdot 10^{-2}$. Since manganese dioxide dissociates in oxygen at 565°C, it may be assumed that the limiting value of 21.0 is reached at that point. Then

$$\underline{C}_p = 13.00 + 3.09 \cdot 10^{-2} \underline{t} + \underline{c}\underline{t}^2 = 21.0 \ (\underline{t} = 565),$$

$$\underline{c} = -2.97 \cdot 10^{-5},$$

$$\underline{C}_p\ (MnO_2) = 13.00 + 3.09 \cdot 10^{-2} t - 2.97 \cdot 10^{-5} t^2,$$

$$\text{or} \quad \underline{C}_p\ (MnO_2) = 1.92 + 4.71 \cdot 10^{-2} \underline{T} - 2.97 \cdot 10^{-5} \underline{T}^2. \qquad \text{(Equation 21)}$$

Thermal and Related Data

General Discussion. - The following figures can be gleaned from the literature on the higher oxides of manganese.

1. MnO_2: Heat of formation, entropy, standard electrode potential, thermal dissociation at high temperatures.
2. Mn_2O_3: no direct data except three determinations of thermal dissociation.
3. Mn_3O_4: Heat of formation and entropy.

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Preliminary calculations show that the data are not entirely consistent with each other. Thus, assuming the figures for MnO_2 to be correct and going through the various steps to arrive at the heat and free energy of Mn_3O_4, the entropy of this last material as calculated from these values differs from the experimental by too large a discrepancy to be ascribable to errors in the entropy determination. Similarly, the converse procedure, starting from Mn_3O_4, and ending with MnO_2, leads to figures for free energy and heat of formation of this latter material which differ too greatly for the error in the entropy of MnO_2.

The procedure that seems best adapted to obtain as good thermodynamic concordance as possible is (a) starting from MnO_2, calculate the properties of Mn_2O_3, (b) starting from Mn_3O_4, calculate similar data for Mn_2O_3, (c) select values for Mn_2O_3 on figures obtained from (a) and (b); (d) using the results of (c), recalculate a revised or adjusted dissociation pressure curve for Mn_3O_4 and MnO_2.

The new dissociation pressures so calculated will differ from both sets of experimental data on this subject but will distribute the errors somewhat and produce free-energy equations that are consistent.

Manganese Dioxide. - In his paper on low-temperature specific heats, Millar (257) reviewed the heats of formation of MnO_2 (Berthelot 125,300, Le Chatelier 126,000, and Mixter 119,600) and selected Berthelot's figure to calculate the free energy of MnO_2. Mixter's work was rejected, apparently because Mixter himself was pessimistic about its accuracy. If, however, the heat of formation of MnO_2 is calculated either by means of the standard electrode potential of MnO_2, or from dissociation pressures as described in the general discussion above, lower values than those of Berthelot or Le Chatelier are obtained, agreeing more nearly with Mixter's figure. It seems better, therefore, to calculate ΔH for MnO_2, rather than to accept the calorimetric data, especially since this latter type of determination is technically difficult in the case of MnO_2 and would require extremely careful analysis of product when determined in a bomb calorimeter.

Many attempts to utilize the manganese dioxide electrode for measuring precise electrode potentials have been made, but unfortunately most of these results are not usable because of the irreversibility of the cells, uncertain liquid junctions, and unsuitable selection of electrolytes. However, Brown and Liebhafsky (41) have recently published measurements which seem reliable, even though a simultaneously appearing article by Popoff, Reddick, and Becker (307) describes the MnO_2 electrode as irreversible. These latter authors say, with reference to the experiments of the former, "The main argument is the preparation and analysis of the manganese dioxide." In spite of the objections raised, it must be admitted that the history and behavior of the cells set up by Brown and Liebhafsky must be regarded as fairly satisfactory, and their result will be accepted here as best available.

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According to these latter authors, a value of +1.236 volts was obtained at 25°C. for the standard potential of the reaction

$$MnO_2 + 4H^+ \rightleftharpoons Mn^{++} + 2H_2O$$

Then ΔF_{298} for the reaction is -1.236 x 2 x 23,074 = -57,050. Using the value for the free energy of the Mn^{++} ion given in a previous part of this work, ΔF_{291} (Mn^{++}) = -52,450, and -56,560 for liquid water at 25°C., in accordance with Lewis and Randall, the difference between the reference temperature for Mn^{++} and for the reaction may be ignored, and $\Delta F_{298}(MnO_2)$ calculated from the above reaction as -108,610 calories.

Then for the reaction

$$Mn + O_2 = MnO_2,$$

S 7.5 49.0 13.9 $\Delta S = -42.4,$

$$\Delta F_{298} = \Delta H_{298} - T\Delta S,$$

$$-10,861 = \Delta H_{298} + 12,650,$$

$$\Delta H_{298} = -121,260.$$

Thermal dissociation of manganese dioxide. - A number of experimental efforts to determine the dissociation pressure of MnO_2 furnish data that may be used to calculate the heat and free energy of Mn_2O_3. Thus Meyer and Rötgers (256) report that MnO_2 dissociates into Mn_2O_3 at 530°C. in air and 565°C. in oxygen, but the process was slow and of doubtful reversibility as far as could be determined by their dynamic method. For the dissociation of Mn_2O_3 into Mn_3O_4, they gave 940 and 1,090° in air and in oxygen, respectively, and were able to show the process reversible. They used MnO_2 prepared from the nitrate, with the correct percentage of active oxygen.

Similarly, Adkenasy and Klonowsky (2) gave a number of points on the dissociation curve disagreeing with Meyer and Rötgers, but they had used precipitated MnO_2. Further, Kendall and Fuchs (201) report a value for pure MnO_2 agreeing with neither of the previously mentioned experimenters.

Honda and Soné (167) determined critical temperatures of structure change by measuring the variation of magnetic susceptibility at various temperatures. Their figures are close to those of Meyer and Rötgers.

The most extensive work on the dissociation of MnO_2 has been done by Drucker and Hüttner (75). These authors show that the dissociation pressure of manganese oxide depends on the purity and history of the material and is reversible in a limited range of temperatures. They obtained many determinations, of which one set, using precipitated MnO_2 and working with excess oxygen pressure up to the very last portion of a determination, is reported to represent the best measurements. Their experiments show that solid solutions of oxides are

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probably not formed, but at low temperatures the water content of hydrated or precipitated MnO_2 cannot be removed without partial decomposition, and at high temperatures the reaction to form Mn_2O_3 becomes irreversible.

In utilizing these various results, recourse may be had to the graphical sigma function method, that is, to make a plot of $\Sigma = -R \ln K + \Delta\Gamma_0 \ln T + \frac{1}{2}\Delta\Gamma_1 T + \frac{1}{6}\Delta\Gamma_2 T^2$, where K is the equilibrium constant or dissociation pressure, R the gas constant, T the absolute temperature, $\Delta\Gamma_0$, $\Delta\Gamma_1$, etc., the coefficients of a polynomial representing the change of heat capacity of the reactions. The points of the Σ function plot should be one straight line whose slope is ΔH_0 of the standard free energy equation. The value of integration constant $I = \frac{\Delta H_0}{T} - \Sigma$.

Table 48 shows the results of such calculation for all usable points on the dissociation pressure curve, as given by the investigators mentioned above. Thus, for the reaction

$$4MnO_2 = 2Mn_2O_3 + O_2,$$

$$2C_p(Mn_2O_3) = 20.66 + 10.3\cdot10^{-2}T - 5.14\cdot10^{-5}T^2 \quad \text{(From equation 19, p. 114)}$$

$$C_p(O_2) = 6.50 + 0.1\cdot10^{-2}T, \quad \text{(Eastman)}$$

$$\text{Sum,} \qquad 27.16 + 10.4\cdot10^{-2}T - 5.14\cdot10^{-5}T^2$$

$$4C_p(MnO_2) = 7.68 + 18.84\cdot10^{-2}T - 11.88\cdot10^{-5}T^2 \quad \text{(From equation 21, p. 115)}$$

$$\text{Difference,} \quad \Delta C_p = 19.48 - 8.44\cdot10^{-2}T + 6.74\cdot10^{-5}T^2. \quad \text{(Equation 22)}$$

$$\Sigma = -R \ln p_{atm.} + 19.48 \ln T - 4.22\cdot10^{-2}T + 1.123\cdot10^{-5}T^2.$$

The dotted line of fig. 9, which shows graphically the disposition of the various points, turns out to have a slope of +16,160 calories, whence I may be calculated from the points at 631°, 666°, and 696°, which lie on the curve, to be +83.57. Then for the reaction

$$\Delta F^o_T = 16{,}160 - 19.48\ T \ln T + 4.22\cdot10^{-2}T^2 - 1.123\cdot10^{-5}T^3 + 83.57\ T,$$

$$\Delta F^o_{298.1} = +11{,}440. \quad \text{(Equation 23)}$$

$$\Delta H_T = 16{,}160 + 19.48\ T - 4.22\cdot10^{-2}T^2 + 2.25\cdot10^{-5}T^3,$$

$$\Delta H_{298.1} = +18{,}816. \quad \text{(Equation 24)}$$

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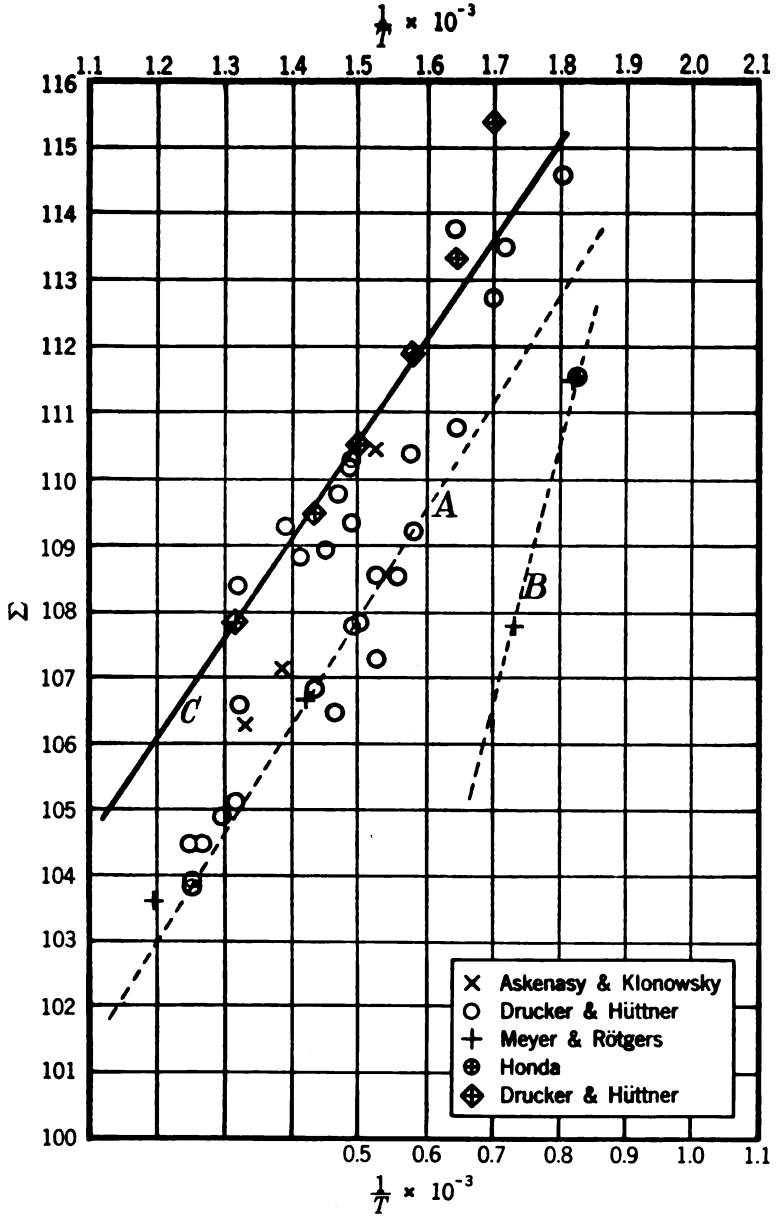

Figure 9.- Sigma function for the dissociation of MnO_2: A, MnO_2- Mn_3O_4; B, MnO_2 - Mn_3O_4; C, MnO_2 - Mn_3O_4.

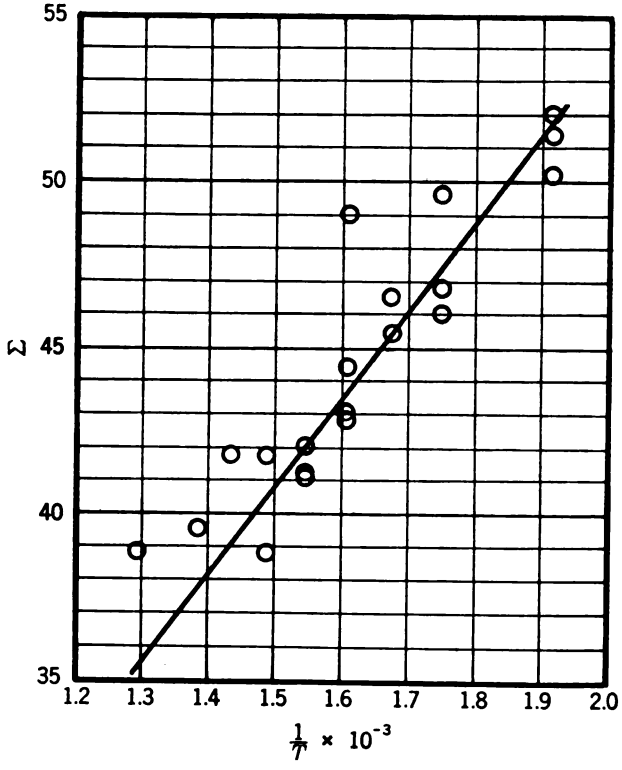

Figure 10.- Sigma function for the reaction $MnCO_3$-MnO+CO_2.

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TABLE 48. - Thermal Dissociation of MnO_2 to Mn_2O_3

Author	Kind of MnO_2	Temperature, °K.	$\frac{1}{T}.10^3$	P_{mm}	P_{atm}	-R ln K	Σ
Askenasy & Klonowsky	Ppt	655	1.527	23.	0.0303	6.955	110.450
do	do	721	1.387	125.	.165	3.587	107.186
do	do	751	1.332	200.	.263	2.652	106.278
Drucker & Hüttner	do	587	1.704	6.6	.0087	9.435	112.715
do	Table 16[1]	606	1.650	18.4	.0242	7.400	110.759
do	do	631	1.585	41.8	.0550	5.763	109.201
do	do	666	1.502	86.2	.1135	4.324	107.839
do	do	696	1.436	150.3	.1975	3.226	106.804
do	do	759	1.318	359.7	.4730	1.488	105.105
Meyer & Rötgers	From nitrate	703	1.423	---	.21	3.102	106.687
do	do	838	1.194	---	1.00	0.000	103.632
Drucker & Hüttner	Table 5[1]	675	1.482	25.4	0.0334	6.758	110.289
do	" 6	801	1.249	502.1	.661	.824	104.468
do	" 7	607	1.647	4.0	.0053	10.415	113.772
do	do	674	1.484	25.0	.0329	6.790	110.310
do	do	718	1.393	43.6	.0574	5.680	109.276
do	do	758	1.320	70.1	.0922	4.740	108.374
do	do	788	1.269	501.5	.659	.828	104.460
do	" 8	581	1.721	4.4	.0058	10.240	113.491
do	do	633	1.580	23.2	.0305	6.940	110.375
do	do	671	1.491	41.6	.0548	5.780	109.311
do	do	682	1.466	47.3	.0623	5.750	109.766
do	do	689	1.452	51.0	.0671	5.365	108.919
do	do	707	1.415	54.1	.0712	5.255	108.834
do	do	756	1.323	252.7	.293	2.440	106.073
do	do	771	1.297	403.7	.531	1.259	104.894
do	do	798	1.253	700	.921	.165	103.806
do	p 253	670	1.493	89.6	.118	4.251	107.780
do	do	654	1.529	78.3	.103	4.517	107.266
do	Table 19[1]	554	1.806	2.4	.0032	11.460	114.591
do	do	641	1.560	59.3	.078	5.068	108.541
do	do	655	1.527	60.2	.079	5.038	108.533
do	do	683	1.465	174.0	.229	2.933	106.478

1 Refers to authors quoted.

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Since $\Delta F = \Delta H - T\Delta S$,

$+11,440 = +18,816 - 293 \cdot \Delta S$,

$\Delta S = +24.4$.

Referring again to the equation of dissociation, and inserting the results of these calculations

$$4MnO_2 = 2Mn_2O_3 + O_2$$

$S = 4 \cdot 13.9 \quad 2x \quad 49.0 \qquad \Delta S = +24.4 \qquad x = 15.5$

$\Delta H \quad 4(-121,260) = 2\Delta H(Mn_2O_3) + 0 \qquad \Delta H(\text{react}) = +18,816$

$\Delta H_{Mn_2O_3} = -233,112$

$\Delta F \quad 4(-108,610) \quad 2\Delta F(Mn_2O_3) + 0 \qquad \Delta F(\text{react}) = +11,440$

$\Delta F_{Mn_2O_3} = -211,500$

As a check on the accuracy of these calculations, consider the entropy of Mn_2O_3 so obtained. Although we have no direct measurements of Mn_2O_3, its entropy is probably not much different from that of Fe_2O_3, for which material Kelley gives $S_{298} = 21.5$. The specific heat of Fe_2O_3 at 0°C. is 23.45 and Mn_2O_3, 23.26; and as the entropies may be taken in rough proportionality, one may estimate $S_{298}(Mn_2O_3) = \frac{23.26}{23.45} \times 21.5 = 21.4$, which differs by some 6 units from that obtained from the dissociation, a discrepancy too great even for this approximate method.

Mangano-Manganic Oxide. - Before similar figures are calculated from the dissociation of Mn_2O_3, the heat and free energy of formation of Mn_3O_4 must be known. Figures for the heat of formation are quoted by Millar (Berthelot and Le Chatelier, both 328,000, Ruff and Gersten, 329,000) but the figure used here will be that of Roth (S19), who reports a heat of formation of 345,000 calories, with a stated uncertainty of only 300 calories. Then for the reaction

$$3Mn + 2O_2 = Mn_3O_4$$

$S = 3 \cdot 7.3 \quad 2 \cdot 49.0 \quad 35.5 \qquad \Delta S = -84.4$

$\Delta F_{298} = \Delta H - T\Delta S$,

$= -345,000 + 298.1 \cdot 84.4$,

$= -319,820$.

Dissociation of Manganic Oxide. - The dissociation pressures measured by Meyer and Rötgers have been given above. Honda's point for dissociation in air is 933 compared to 940 for the former authors. To maintain analogy with the MnO_2 dissociation, the Σ' function is again calculated, even though the small number of points hardly justify the use of the method. The data are shown in table 49.

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Thus, the reaction is

$$6Mn_2O_3 = 4Mn_3O_4 + O_2$$

$4C_p(Mn_3O_4) = 77.00 + 21.52\cdot10^{-2}T - 8.36\cdot10^{-5}T^2$ (From equation 20)

$C_p(O_2) = 6.50 + 0.10\cdot10^{-2}T$ (Eastman)

Sum $83.50 + 21.62\cdot10^{-2}T - 8.36\cdot10^{-5}T^2$

$6C_p(Mn_2O_3) = 61.98 + 31.80\cdot10^{-2}T - 15.42\cdot10^{-5}T^2$ (From equation 19)

Difference $= \Delta C_p = 21.52 - 10.18\cdot10^{-2}T + 7.06\cdot10^{-5}T^2$

$$\Sigma = -R \ln p_{atm.} + 21.52 \ln T - 5.09\cdot10^{-2}T + 1.177\cdot10^{-5}T^2.$$

The slope of the dotted line through the points of the Σ-function plot of figure 10, representing the data on Mn_2O_3, is $\Delta H_o = 40,650$, whence $I = 77.97$. Then for the reaction

$$\Delta F^o_T = 40,650 - 21.52\ T \ln T + 5.09\cdot10^{-2}T^2 + 1.177\cdot10^{-5}T^3 + 77.97\ T. \quad \text{(Equation 25)}$$

$\Delta F_{298} = +32,185,$

$$\Delta H_T = 40,650 + 21.52\ T - 5.09\cdot10^{-2}T^2 - 2.35\cdot10^{-5}T^3. \quad \text{(Equation 26)}$$

$\Delta H_{298} = +41,923,$

$$\Delta S_{298} = \frac{\Delta H - \Delta F}{T} = \frac{9,273}{298} = +31.1.$$

TABLE 49. - Dissociation of Manganic Oxide

Author	Temperature °C.	Temperature °K.	$\frac{1}{T}\cdot10^3$	$p_{atm.}$	$-R \ln K$	Σ
Meyer & Rotgers.....	940	1,213	0.8244	0.21	3.102	111.486
do.....	1,090	1,363	.7337	1.00	.000	107.794
Honda.....	933	1,206	.8292	.21	3.102	111.520

Referring again to the decomposition reaction, and inserting the known results above to calculate the properties of Mn_2O_3, there results

	$6Mn_2O_3$	$= 4Mn_3O_4$	$+ O_2$	
S_{298}	$6x$	$4\cdot35.5$	49.0	$\Delta S = 31.1$, $x = S_{298}(Mn_2O_3) = 26.6$
ΔH	$6\Delta H(Mn_2O_3)$	$4(-345,000)$	0	ΔH(react) $= +41,923$ $\Delta H_{298}(Mn_2O_3) = -236,987$
ΔF	$6\Delta F(Mn_2O_3)$	$4(-319,820)$	0	ΔF(react) $= +32,185$ $\Delta F_{298}(Mn_2O_3) = -218,577$

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The figures so obtained are to be compared with similar ones obtained from the dissociation of MnO_2. It is apparent that the entropy is now 5.2 units too high, if 21.4 may be assumed correct. The two results for $\Delta \underline{H}$ (-236,987 and -233,112), if averaged, give the figure which will be selected, $\Delta \underline{H}_{298}(Mn_2O_3)$ = -235,050, and the average of the $\Delta \underline{F}$ figures (-211,500 and -218,577 is $\Delta \underline{F}_{298}$ (Mn_2O_3) = -215,040. Finally, for the formation of Mn_2O_3, since

$$\Delta \underline{S} = \frac{\Delta \underline{H} - \Delta \underline{F}}{\underline{T}} = \frac{-20,010}{298} = -67.1,$$

$$2Mn + \tfrac{3}{2}O_2 = Mn_2O_3$$

$$\underline{S} = 2 \cdot 7.3 \quad \tfrac{3}{2} \cdot 49.0 \quad \underline{x}, \qquad \Delta \underline{S} = -67.1$$

$$\underline{x} = \underline{S}_{298}(Mn_2O_3) = 21.0.$$

The selection of the average values above results in an entropy of Mn_2O_3 only 0.4 unit different from that estimated from Fe_2O_3, and represents a degree of thermodynamic consistency that is about all that could be expected in view of the nature of the data.

Standard Free-Energy Equations for Higher Oxides.

The information obtained from the rather involved calculations which have just been made enable standard free-energy equations to be constructed for the formation and dissociation of higher oxides which do not lead to thermodynamic inconsistencies, at least as far as entropy is concerned, and which undoubtedly furnish the best interpretation of the data now existing. In view of the experimental difficulties, and the poor reversibility of some dissociation reactions, this interpretation is thought to be better in this respect than the actual determinations made.

Proceeding now to the individual cases, for the reaction

$$2Mn_{(\alpha)} + \tfrac{3}{2}O_2 = Mn_2O_3$$

$$\underline{C}_p(Mn_2O_3) = 10.33 + 5.3 \cdot 10^{-2}\underline{T} - 2.57 \cdot 10^{-5}\underline{T}^2 \qquad (1)$$

$$\underline{C}_p(2Mn\alpha) = 7.56 + 1.48 \cdot 10^{-2}\underline{T} \qquad (2)$$

$$\underline{C}_p(\tfrac{3}{2}O_2) = 9.75 + .15 \cdot 10^{-2}\underline{T} \qquad (3)$$

$$\text{Sum of (2 \& 3)} = 17.31 + 1.63 \cdot 10^{-2}\underline{T}$$

$$\text{Difference} = \Delta \underline{C}_p = -6.98 + 3.67 \cdot 10^{-2}\underline{T} - 2.57 \cdot 10^{-5}\underline{T}^2$$

$$\Delta \underline{H}_{298} = -235,050 = \Delta \underline{H}_o - 6.98\ \underline{T} + 1.83 \cdot 10^{-2}\underline{T}^2 - 0.857 \cdot 10^{-5}\underline{T}^2, \quad \Delta \underline{H} = -234,370,$$

$$\Delta \underline{H}_T = -234,370 - 6.98\ \underline{T} + 1.83 \cdot 10^{-2}\underline{T}^2 - 0.857 \cdot 10^{-5}\underline{T}^2. \qquad \text{(Equation 27)}$$

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$\Delta F_{298} = -215,040 = -234,370 + 6.98\ T \ln T - 1.83\cdot10^{-2}T^2 + 0.428\cdot10^{-5}T^3 + I\ T,$

$I = +30.15,$

$\Delta F^{o}_{T} = -234,370 + 6.98\ T \ln T - 1.83\cdot10^{-2}T^2 + 0.428\cdot10^{-5}T^3 + 30.15\ T.$ (Equation 28)

Furthermore, from Mn_3O_4 there is obtained

$3Mn_{(\alpha)} + 2O_2 = Mn_3O_4$

$C_p(Mn_3O_4) = 19.25 + 5.38\cdot10^{-2}T - 2.09\cdot10^{-5}T^2$ (1)

$C_p(3Mn\alpha) = 11.34 + 2.21\cdot10^{-2}T$ (2)

$C_p(2O_2) = 13.00 + .20\cdot10^{-2}T$ (3)

Sum of (2 & 3) $24.34 + 2.41\cdot10^{-2}T,$

Difference $= \Delta C_p = -5.09 + 2.97\cdot10^{-2}T - 2.09\cdot10^{-5}T^2,$

$\Delta H_{298} = -345,000 = \Delta H_o - 5.09\ T + 1.485\cdot10^{-2}T^2 - 0.665\cdot10^{-5}T^3,\ \Delta H_o = -344,627,$

$\Delta H_T = -344,627 - 5.09\ T + 1.485\cdot10^{-2}T^2 - 0.665\cdot10^{-5}T^3.$ (Equation 29)

$\Delta F_{298} = -319,820 = -344,627 + 5.09\ T \ln T - 1.485\cdot10^{-2}T^2 + 0.322\cdot10^{-5}T^3 + I\ T,$

$I = +58.35,$

$\Delta F^{o}_{T} = -344,627 + 5.09\ T \ln T - 1.485\cdot10^{-2}T^2 + 0.332\cdot10^{-5}T^3 + 58.35\ T.$ (Equation 30)

Finally, for the formation of MnO_2, according to the reaction

$Mn\alpha + O_2 = MnO_2,$

$C_p(MnO_2) = 1.92 + 4.71\cdot10^{-2}T - 2.97\cdot10^{-5}T^2$ (1)

$C_p(Mn\alpha) = 3.78 + 0.74\cdot10^{-2}T$ (2)

$C_p(O_2) = 6.50 + 0.10\cdot10^{-2}T$ (3)

Sum of (2 & 3) $= 10.28 + 0.84\cdot10^{-2}T,$

Difference $= \Delta C_p = -8.36 + 3.87\cdot10^{-2}T - 2.97\cdot10^{-5}T^2,$

$\Delta H_{298} = -121,260 = \Delta H_o - 8.36\ T + 1.94\cdot10^{-2}T^2 - 0.99\cdot10^{-5}T^3,$

$\Delta H_o = -120,230,$

$\Delta H_T = -120,230 - 8.36\ T + 1.94\cdot10^{-2}T^2 - 0.99\cdot10^{-5}T^3.$ (Equation 31)

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$\Delta F_{298} = -108,610 = -120,230 + 8.36\ T \ln T - 1.94\cdot10^{-2}T^2 + 0.495\cdot10^{-5}T^3 + I\ T,$

$I = -3.31,$

$\Delta F^{o}_{T} = -120,230 + 8.36\ T \ln T - 1.94\cdot10^{-2}T^2 + 0.495\cdot10^{-5}T^3 - 3.31\ T.$ (Equation 32)

In the case of the dissociation of MnO_2 into Mn_2O_3, the change of specific heat and preliminary standard free-energy equations have already been given, so there only remains the necessary modification to accommodate the finally selected figures for Mn_2O_3.

$$4MnO_2 = 2Mn_2O_3 + O_2$$

ΔH_{298}	4(-121,260)	2(-235,050)	0	$\Delta H = +14,940$
ΔF_{298}	4(-108,610)	2(-215,040)	0	$\Delta F = +4,360$

$\Delta H_{298} = +14,940 = \Delta H_o + 19.48\ T - 4.22\cdot10^{-2}T^2 + 2.25\cdot10^{-5}T^3,$

$\Delta H_o = +12,296,$

$\Delta H_T = +12,296 + 19.48\ T - 4.22\cdot10^{-2}T^2 + 2.25\cdot10^{-5}T^3.$ (Equation 33)

$\Delta F_{298} = +4,360 = +12,296 - 19.48\ T \ln T + 4.22\cdot10^{-2}T^2 - 1.123\cdot10^{-5}T^3 + I\ T,$

$I = +72.8,$

$\Delta F^{o}_{T} = +12,296 - 19.48\ T \ln T + 4.22\cdot10^{-2}T^2 - 1.123\cdot10^{-5}T^3 + 72.8\ T.$ (Equation 34)

Similarly, for the reaction

$$6Mn_2O_3 = 4Mn_3O_4 + O_2$$

ΔH_{298}	6(-235,050)	4(-345,000)	0	$\Delta H = +30,300$
ΔF_{298}	6(-215,040)	4(-319,820)	0	$\Delta F = +10,960$

$\Delta H_{298} = +30,300 = \Delta H_o + 21.52\ T - 5.09\cdot10^{-2}T^2 - 2.35\cdot10^{-5}T^3,\ \Delta H = +29,027,$

$\Delta H_T = +29,027 + 21.52T - 5.09\cdot10^{-2}T^2 - 2.35\cdot10^{-5}T^3.$ (Equation 35)

$\Delta F_{298} = +10,960 + 29,027 - 21.52\ T \ln T + 5.09\cdot10^{-2}T^2 + 1.177\cdot10^{-5}T^3 + I\ T,$

$I = +45.67,$

$\Delta F^{o}_{T} = +29,027 - 21.52\ T \ln T + 5.09\cdot10^{-2}T^2 + 1.177\cdot10^{-5}T^3 + 45.67\ T.$ (Equation 36)

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If now one proceeds to calculate dissociation pressures for MnO_2 and Mn_2O_3 from equations 34 and 36, the results so obtained at any temperature are much higher than the observed experimental ones. To obtain thermodynamic consistency it has become necessary to assume that the experimental dissociation pressures are incorrect.

The discrepancy so disclosed leads one to a hypothetical assumption that the dissociations actually occurring were not in fact those whose equations were written. Thus, for example, one might suppose that MnO_2 dissociated to MnO, or Mn_3O_4, instead of Mn_2O_3.

The necessary calculations for the reaction $2MnO_2 = 2MnO + O_2$ were carried through, assuming the properties of MnO_2 to be correct and calculating from the observed dissociation pressures what the entropy of MnO would be if this actually were the reaction. Without reproducing here the actual figures involved, it may merely be stated that the entropy of MnO_2 calculated in this way turns out to be less than 2 units, an obviously impossible condition.

In contrast to this, calculations for the second hypothesis show an almost satisfactory condition. In the reaction

$$3\,MnO_2 = Mn_3O_4 + O_2$$

$$\underline{C}_p(Mn_3O_4) = 19.25 + 5.38\cdot10^{-2}\underline{T} - 2.09\cdot10^{-5}\underline{T}^2$$

$$\underline{C}_p(O_2) = 6.50 + 0.10\cdot10^{-2}\underline{T}$$

$$\text{Sum} = 25.75 + 5.48\cdot10^{-2}\underline{T} - 2.09\cdot10^{-5}\underline{T}^2$$

$$\underline{C}_p(3MnO_2) = 5.76 + 14.13\cdot10^{-2}\underline{T} - 8.91\cdot10^{-5}\underline{T}^2$$

$$\text{Difference} = \Delta\underline{C}_p = 19.99 - 8.65\cdot10^{-2}\underline{T} + 6.82\cdot10^{-5}\underline{T}^2$$

The Σ function is then

$$\Sigma = -\underline{R}\,\underline{\ln}\,\underline{p} + 19.99\,\underline{\ln}\,\underline{T} - 4.325\cdot10^{-2}\underline{T} + 1.137\cdot10^{-5}\underline{T}^2.$$

Table 50 shows the individual points for the "best" results of Drucker and Huttner (75). The slope of the middle points which more closely represent a straight line is $\Delta\underline{H}_0 = +14{,}930$. Then

$$\Delta\underline{H}_{\underline{T}} = 14{,}930 + 19.99\,\underline{T} - 4.325\cdot10^{-2}\underline{T}^2 + 2.27\cdot10^{-5}\underline{T}^2,$$

$$\Delta\underline{H}_{298} = +18{,}649,$$

$$\Delta\underline{F}^{\circ}_{\underline{T}} = +14{,}930 - 19.99\,\underline{T}\,\underline{\ln}\,\underline{T} + 4.325\cdot10^{-2}\underline{T}^2 - 1.137\cdot10^{-5}\underline{T}^3 + 88.18\,\underline{T},$$

$$\Delta\underline{F}_{298} = +10{,}842.$$

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If similar figures are calculated from the accepted heats and free energies of the components

	$3MnO_2$	=	Mn_3O_4	+	O_2	
ΔH	3(-121,260)		-34,500		0	ΔH_{298} = +18,780
ΔF	3(-108,610)		-319,820		0	ΔF_{298} = +6,010

These values, +18,780 and +6,010 calories for heat and free energy, compare not too badly with +18,649 and +10,842, calculated from the assumed dissociation of MnO_2 in Mn_3O_4, using dissociation pressures, and because the heats of reaction check so well there is a considerable incentive to assume that MnO_2 really dissociated into Mn_3O_4 in the decomposition experiments. However, Drucker and Huttner made X-ray measurements of pure Mn_2O_3 and of their partly dissociated dioxide, and their evidence seems to prove very definitely that not Mn_3O_4, but Mn_2O_3, is formed. It is unfortunate that they did not also determine the X-ray pattern of Mn_3O_4, since such tests would have definitely settled the matter. It should also be stated, however, that if the values 18,780 and 6,010, calculated from MnO_2 and Mn_3O_4, are used to set up a free-energy equation, the hypothetical decomposition pressures so calculated are considerably higher than the observed. The multiplicity of atoms and molecules involved renders such calculation very sensitive to small errors, but the behavior of the MnO_2 in the dissociation experiments indicates that the true dissociation pressure may be higher than that measured, because it was found that even a small amount of decomposition lowered the observed pressure.

In conclusion, it must be admitted that the question of the dissociation of the higher oxides of manganese is still in a very unsatisfactory condition from a thermodynamic viewpoint. Some crucial experiment which will definitely confirm one of the various hypotheses that have been advanced is greatly needed. Until that time, perhaps the best that can be done is to assume that the dissociation experiments are unreliable and that the processes are probably irreversible.

TABLE 50. - Σ Function for Reaction

$3MnO_2 = Mn_3O_4 + O_2$ (Drucker and Huttner data)

Temperature, °K.	$\frac{1}{T}.10^3$	$-R \ln p$	Σ
587	1.704	9.435	115.394
606	1.650	7.400	113.340
631	1.585	5.763	111.882
666	1.502	4.324	110.514
696	1.436	3.226	109.489
759	1.318	1.488	107.839

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MANGANESE SULPHIDE

Physical Properties

Manganese sulphide occurs in nature as the mineral alabandite and crystallizes in the cubic system; density, about 4.0. According to Shibata (346) it melts at 1,610 ± 3° C.

Specific Heats

The only available specific heats for manganese sulphide at low temperatures are those of Anderson (6), who gives for the entropy $S_{298}(MnS) = 18.7 \pm 0.3$. Manganese sulphide has a very pronounced and peculiarly shaped anomaly in the specific heat curve in the neighborhood of 125°-140°K. Nothing is known as yet concerning the validity of entropy data obtained by determining the anomalous area. Since MnO, MnO_2, and MnS all have "humps" in the specific heat at low temperatures, these materials offer an excellent opportunity to check the effect of such peculiarities if adequate chemical data could be secured.

The only figure for high-temperature specific heats of MnS is that of Stella (355), who gives 0.1392 per gram, or 12.1 per gram-formula weight of MnS. Under these circumstances the best that can be done for high-temperature specific heats of MnS is an estimate similar in method to that used for the oxides of manganese.

Thus by plotting Anderson's data in the neighborhood of 0°C.,

$\underline{a} = \underline{C_p}$ at 0°C. = 11.82, $\underline{b} = \left(\frac{d\underline{C_p}}{dt}\right)_{\underline{t}=0} = 5.24 \cdot 10^{-3}$, $\underline{C_p}$ at 1,610 = 14.0,

$\underline{c} = -2.42 \cdot 10^{-6}$, and

$$\underline{C_p}(MnS) = 11.82 + 5.24 \cdot 10^{-3}\underline{t} - 2.42 \cdot 10^{-6}\underline{t}^2,$$

or $\underline{C_p}(MnS) = 10.21 + 6.56 \cdot 10^{-3}\underline{T} - 2.42 \cdot 10^{-6}\underline{T}^2$. (Equation 37)

Thermal and Related Data

Older determinations of the heat of formation of MnS obtained by precipitation methods are those of Thomsen (369), who reported 44,390 calories for a hydrous sulphide from sulphate solution, and Berthelot (24), who obtained 45,600 calories for the sulphide precipitated from the acetate solution. These values are in complete disagreement with the direct determinations of Wologdine and Penkiewitsch (395), who attempted to measure directly the heat of formation by igniting a mixture of powdered manganese and sulphur in a bomb under nitrogen pressure and obtained 62,900 calories. Many recent investigators have shown that nitrogen combines directly with manganese even at relatively low ignition temperatures, but even this obvious source of error in these experiments cannot account for the large discrepancy. Reference to their original article discloses a none too careful method of analysis of resulting sulphide and considerable vagueness in regard to the rather large corrections applied for the igniting powder of aluminum and potassium chlorate.

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By thermodynamic means, values for the heat of formation of MnS may be calculated from other data, which confirm the magnitude of the results of Thomsen and Berthelot; in furtherance of these calculations the value of Berthelot is accepted tentatively.

As first attempt to calculate the heat of formation of MnS, consider the solubility data of Weigel (382), who obtained $54.5 \cdot 10^{-6}$ moles per liter for the solubility from conductivity experiments at 18°C. To calculate the solubility from his measurements of conductivity, Weigel assumed complete hydrolysis of the MnS, but it seems more probable that the actual solution may be better expressed by the equation

$$MnS + H_2O = Mn^{++} + HS^- + OH^-.$$

He made some measurements of the conductivity of H_2S solutions to show that his calculation was correct, but a simple calculation shows that the HS^- ion exists in relatively large proportion. Thus, if the molal concentration of $Mn(OH)_2$ from the hydrolysis of sulphide were $5.45 \cdot 10^{-5}$, as determined by Weigel, then (OH^-) is approximately $1 \cdot 10^{-4}$, and since $(H^+)\ (OH^-) = 10^{-14}$, $(H^+) = 10^{-10}$, the equilibrium constant for the first dissociation of $H_2S \rightarrow H^+ + HS^-$ is roughly 10^{-7}, then

$$\frac{(H^+)\ (HS^-)}{(H_2S)} = 10^{-7}, \qquad \frac{(HS^-)}{H_2S} = \frac{10^{-7}}{10^{-10}} = 10^3.$$

In view of these conditions, the measurements of Weigel will be recalculated.

It was found that the increase of conductivity due to MnS (green) was $23.38 \cdot 10^{-6}$; then the molal concentration of MnS, assuming complete dissociation into Mn^{++}, HS^-, and OH^- ions, is

$$\underline{c} = \frac{1{,}000 \cdot 23.38 \cdot 10^{-6}}{2.45 + 174 + 62} = 7.16 \cdot 10^{-5},$$

where 45 has been taken for the ion mobility of $\frac{1}{2}\ Mn^{++}$, 174 for OH^-, and 62 for HS^-. (Note that the value $7.16 \cdot 10^{-5}$ refers to the green sulphide, and it is only fortuitous that Weigel calculated $71.60 \cdot 10^{-6}$ for the flesh-colored sulphide.

Then for the reaction attending solution of the MnS,

$$\underline{K} = (Mn^{++})\ (HS^-)\ (OH^-) = (7.16 \cdot 10^{-5})^3,$$

$$= 3.67 \cdot 10^{-13},$$

and $\Delta \underline{F} = -\underline{RT}\ \ln \underline{K} = -4.578 \cdot 291 \cdot (-12.435)$,

$$= +16{,}560.$$

Further, if one ignores the difference in reference temperatures, and again writes the reaction

$$MnS + H_2O = Mn^{++} + HS^- + OH^-,$$

$$\Delta \underline{F} \quad \underline{x} \quad -56{,}560 \quad -52{,}450 \quad +2{,}980 \quad -37{,}455 \quad \Delta \underline{F} = +16{,}560,$$

$$\underline{x} = -47{,}025.$$

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The values for H_2O, HS^-, and OH^- are those of Lewis and Randall, that for Mn^{++} being given in an earlier part of this work.

Finally, assuming that -47,025 is the free energy at 298, one may write

$$Mn(\alpha) + S(rh) = MnS$$

$$\underline{S}_{298} \quad 7.3 \qquad 7.6 \qquad 18.7 \qquad \Delta\underline{S} = +3.8$$

$$\Delta\underline{F} = \Delta\underline{H} - \underline{T}\Delta\underline{S},$$

$$-47,025 = \Delta\underline{H} - 1,135,$$

$$\Delta\underline{H} = -45,890.$$

This result must be regarded as a fortuitous check with Berthelot's -45,600 but confirms the order of magnitude.

As a second check, the work of Guntz (129) may be used. This experimenter found that pyrophoric manganese reacted with SO_2 to give MnS and MnO and was converted to manganese hydroxide with the evolution of 98,600 calories. If from this last figure one subtracts Roth's heat of formation of oxide, 96,500, a "correction" term of 2,100 is found for the "pyrophoric" manganese, if the heat of hydration of the oxide is ignored. So in the reaction

$$3Mn(pyro) + SO_2 = MnS + 2MnO,$$

$$\Delta\underline{H} \quad 3\cdot 2,100 \qquad -70,940 \qquad x \qquad 2(-96,500) \qquad \Delta\underline{H} = -82,400$$

$$\Delta\underline{H}(MnS) = \underline{x} = -46,160.$$

In the equation above, the SO_2 value is a recent one of Eckman and Rossini (80). Here again a very satisfactory confirmation of Berthelot's older value for MnS is found.

As a final check on the heat of formation of MnS, reference may be made to some experiments of Jellinek and Von Podjaski (179). These experiments will be considered in detail later in connection with the thermodynamic properties of manganese chloride. Mention will be merely made here that the slopes of their equilibrium data lead to a value of heat of reaction which could only be obtained from a value of heat of formation of MnS corresponding to the figures given above by Berthelot.

In writing the standard free-energy equation for the formation of MnS, the value $\Delta\underline{H}_{298} = -45,890$ will be taken, as representing the mean of the three good results discussed above. Then $\Delta\underline{F}_{298} = -47,025$. Therefore the reaction

$$Mn(\alpha) + S(rh) = MnS.$$

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$$\underline{C}_p(\text{MnS}) = 10.21 + 6.56\cdot10^{-3}\underline{T} - 2.42\cdot10^{-6}\underline{T}^2$$

$$\underline{C}_p(\text{Mn }\alpha) = 3.78 + 7.38\cdot10^{-3}\underline{T}$$

$$\underline{C}_p(\text{S rh}) = \frac{4.12 + 4.70\cdot10^{-3}\underline{T}}{7.90 + 12.08\cdot10^{-3}\underline{T}} \qquad \text{(Lewis \& Randall)}$$

$$\text{Sum}$$

$$\text{Difference} = \Delta\underline{C}_p = 2.31 - 5.52\cdot10^{-3}\underline{T} - 2.42\cdot10^{-6}\underline{T}^2$$

$$\Delta\underline{H}_{298} = -45{,}890 = \Delta\underline{H}_o + 2.31\ \underline{T} - 2.76\cdot10^{-3}\underline{T}^2 - 0.81\cdot10^{-6}\underline{T}^3. \qquad \text{(Equation 38)}$$

$$\Delta\underline{H}_o = -46{,}313,$$

$$\Delta\underline{F}^o_{298} = -47{,}025 = -46{,}313 - 2.31\ \underline{T}\ \underline{\ln}\ \underline{T} + 2.76\cdot10^{-3}\underline{T}^2 + 0.403\cdot10^{-6}\underline{T}^3 + \underline{I}\ \underline{T},$$

$$\underline{I} = +9.90,$$

$$\Delta\underline{F}^o_{\underline{T}} = -46{,}313 - 2.31\ \underline{T}\ \underline{\ln}\ \underline{T} + 2.76\cdot10^{-3}\underline{T}^2 + 0.403\cdot10^{-6}\underline{T}^3 + 9.90\ \underline{T}.$$

(Equation 39)

Liquid Manganese Sulphide

There are no direct determinations of the heat of fusion of MnS, but since the important metallurgical use of manganese as a desulphurizer involves liquid sulphide, it may be worth while to make a very approximate estimate of the properties of liquid MnS.

If one attempts to calculate the heat of fusion from the melting points of the FeS - MnS system, using the data of Shibata (346), absurd results are obtained.

As an alternative, the assumption may be made that the entropy of fusion of MnS is the same as FeS. For the latter material, there is available a single approximate measurement of Bornemann and Hengstenberg (30), corresponding to 60 calories per gram or 5,270 calories per FeS. Since the melting point is 1,173°C. the entropy of fusion is 3.64 units; and the heat of fusion of MnS, melting at 1,610°C. is estimated at 6,850 calories per MnS.

A very crude guess at the specific heat of liquid MnS would be 16 calories per formula weight.

MANGANESE CARBONATE

Manganese carbonate occurs in nature as the mineral rhodochrosite, with a density of approximately 3.5, crystallizing in rhombohedra isomorphous with calcite. No allotropic forms have been reported.

Specific Heats

The specific heats of the natural mineral have recently been determined throughout the low-temperature range by Anderson (7), who reports for the entropy $\underline{S}_{298} = 20.52 \pm 0.4$.

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For the high-temperature range no data are available, and the specific heat must be estimated in the same manner as used previously in this work. Thus, from the value taken from Anderson's curve at

$$\underline{t} = 0^{\circ}C., \quad \underline{a} = \underline{C_p}273.1 = 18.62, \quad \underline{b} = \left(\frac{\partial \underline{C_p}}{\partial \underline{T}}\right)_{\underline{T}=273.1} = 3.72 \cdot 10^{-2},$$

Further, since $MnCO_3$ reaches a dissociation pressure of 1 atmosphere near 500°C. and assuming that $\underline{C_p} = 35$ at that temperature,

$$\underline{c} = -0.9 \cdot 10^{-5}.$$

Then $\underline{C_p}MnCO_3 = 18.62 + 3.72 \cdot 10^{-2}\underline{t} - 0.9 \cdot 10^{-5}\underline{T}^2$,

or $\underline{C_p}(MnCO_3) = 7.79 + 4.21 \cdot 10^{-2}\underline{T} - 0.9 \cdot 10^{-5}\underline{T}^2$.

Thermal and Dissociation Data

The older value of Thomsen for the heat of formation of $MnCO_3$, 210,840 calories, is regarded as much less certain than the recent results of Roth (319), who gives for the formation from its elements, 219,100± 800 calories, and for the reaction

$$MnO + CO_2 = MnCO_3, \qquad \Delta\underline{H} = -28,300 \pm 800.$$

The free energy of $MnCO_3$ may be calculated from the third law as follows:

$$Mn(\alpha) + C + \tfrac{3}{2}O_2 = MnCO_3,$$

$\underline{S}_{298}$	7.3	1.3	73.5	20.5	$\Delta\underline{S} = 61.6$

$$\Delta\underline{F}^{o}_{298} = \Delta\underline{H}_{298} - \underline{T}\Delta\underline{S}_{298},$$

$$= -219,100 + 18,220,$$

$$= -200,880.$$

The figure so obtained may be checked by comparison with dissociation data for $MnCO_3$, which have been determined experimentally by Manchot and Lorenz. As before, it will be desirable to set up a Σ function plot for the experimental data. Thus for the reaction

$$MnCO_3 = MnO + CO_2$$

$$\underline{C_p}(MnO) = 7.43 + 1.04 \cdot 10^{-2}\underline{T} - 0.362 \cdot 10^{-5}\underline{T}^2$$

$$\underline{C_p}(CO_2) = 7.70 + 0.53 \cdot 10^{-2}\underline{T} - 0.083 \cdot 10^{-5}\underline{T}^2$$

$$\text{Sum} \quad 15.13 + 1.57 \cdot 10^{-2}\underline{T} - 0.445 \cdot 10^{-5}\underline{T}^2$$

$$\underline{C_p}(MnCO_3) = 7.79 + 4.21 \cdot 10^{-2}\underline{T} - 0.90 \cdot 10^{-5}\underline{T}^2$$

$$\text{Difference} = \Delta\underline{C_p} = 7.34 - 2.64 \cdot 10^{-2}\underline{T} + 0.455 \cdot 10^{-5}\underline{T}^2$$

$$\Sigma = -\underline{R}\ \underline{\ln}\ \underline{p} + 7.34\ \underline{\ln}\ \underline{T} - 1.32 \cdot 10^{-2}\underline{T} + 0.076 \cdot 10^{-5}\underline{T}^2.$$

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Table 51 shows the specific figures based on the various experiments of Manchot and Lorenz, and the corresponding chart of Σ v. $\frac{1}{T}$ appears in figure 10. These authors showed that the equilibrium between carbonate, oxide, and CO_2 was only moderately reversable.

TABLE 51. - Σ Function for Thermal Dissociation of $MnCO_3$

($\Sigma = -R \ln p + 7.34 \ln T - 1.32 \cdot 10^{-2} T + 0.76 \cdot 10^{-6} T^2$)

Series	Temperature, °C.	Temperature, °K.	$\frac{1}{T} \cdot 10^3$	Pmm	Patm	$-R \ln p$	Σ
A.....	250	523	1.913	1.6	0.0021	+12.25	51.45
	300	573	1.746	4.0	.0053	+10.42	49.69
	350	623	1.606	5.5	.0072	+9.79	49.08
	500	773	1.294	855.	1.125	-.23	38.81
B.....	250	523	1.913	3.	.0040	+11.02	50.22
	300	573	1.746	25.	.0329	+6.79	46.06
	325	598	1.672	35.	.0461	+6.12	45.45
	350	623	1.605	127.	.167	+3.56	42.85
	375	648	1.544	286.	.376	+1.95	41.25
	400	673	1.486	855.	1.125	-.23	38.81
C.....	350	623	1.605	115.	.151	+3.75	43.04
	375	648	1.544	303.	.399	+1.83	41.13
D.....	250	523	1.913	7.5	.0099	+9.18	52.06
	300	573	1.746	17.0	.0224	+7.56	46.83
	325	598	1.672	20.0	.0263	+7.23	46.56
	350	623	1.605	57.0	.0750	+5.15	44.44
	375	648	1.544	113.	.149	+3.79	43.09
	400	673	1.486	198.	.261	+2.67	41.71
	425	698	1.432	221.	.291	+2.45	41.71
	450	723	1.384	650.	.856	+0.31	39.53

The line drawn in the figure has this slope, passing through those points which seem from the experimental data to be best. Then the value of I for the free-energy equation is found to be -0.1, and the free energy of dissociation is given by the expression

$$\Delta F^{o}_{T} = +27,245 - 7.34\ T \ln T + 1.32 \cdot 10^{-2} T^2 - 0.76 \cdot 10^{-6} T^3 - 0.1\ T,$$

$$\Delta F^{o}_{298} = +15,913.$$

This final result may be compared with that calculated directly

$$MnCO_3 = MnO + CO_2.$$

$$\Delta F_{298} \quad -200,880 \quad -91,310 \quad -93,650 \qquad \Delta F_{298} = +15,920.$$

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The concordance here between the two values of free energy is, of course, much better than could have been expected from the nature of the equilibrium data.

As a final check on the free energy of formation of $MnCO_3$, one may utilize the measurements of the solubility of this material in solutions containing carbon dioxide. Thus, Haehnel (142) found that when the partial pressure of CO_2 was 1 atmosphere, 0.04 percent $MnCO_3$ was dissolved at 18°C., and when the pressure was 56 atmospheres, 0.08 percent was so dissolved. The corresponding molal concentrations of $MnCO_3$ are $3.48 \cdot 10^{-3}$, and $6.96 \cdot 10^{-3}$. Further, one may write $K = \frac{\alpha (MnHCO_3)^2}{(H_2CO_3)^3}$, where α is the dissociation of manganous bicarbonate. In this case, because of the low concentrations involved, α may be assumed equal to unity. The solubility product of $MnCO_3$, $K_3 = (Mn^{++})\ (CO_3^{--})$ is related to K by the expression $K_3 = \frac{K^3 (4K_2)}{K_1}$, where K_1 and K_2 are the first and second dissociation constants for carbonic acid. Lewis and Randall give $K_1 = 350 \cdot 10^{-7}$, $K_2 = 3.7 \cdot 10^{-11}$ at 25°. We shall have to assume that the difference between the ratio $\frac{4K_2}{K}$ at 25 and 18° is negligible, since more specific information is lacking. The solubility of CO_2 at 18° is 0.0414 molal when the pressure is 1 atmosphere and 1.25 molal at 56 atmospheres.

Then $$K_{(1\ atm)} = \frac{(3.48 \cdot 10^{-3})^2}{(4.14 \cdot 10^{-2}) 1/3} = 3.5 \cdot 10^{-5},$$

and $$K_{(56\ atm)} = \frac{(6.96 \cdot 10^{-3})^2}{(1.25) 1/3} = 4.48 \cdot 10^{-5}.$$

Further, $$K_{3(1\ atm)} = \frac{(3.5 \cdot 10^{-5})^3 \cdot 14.8 \cdot 10^{-11}}{350 \cdot 10^{-7}},$$

$$= 1.81 \cdot 10^{-19},$$

$$K_{3(56\ atm)} = \frac{(4.48 \cdot 10^{-5})^3 \cdot 14.8 \cdot 10^{-11}}{350 \cdot 10^{-7}},$$

$$= 4.66 \cdot 10^{-19}.$$

For the reaction $MnCO_3 = Mn^{++} + CO_3^{--}$,

$\Delta F_{291} = -R\ T\ \ln\ K_3 = +24{,}950$ at 1 atmosphere and $+24{,}400$ at 56 atmospheres

If the difference in free energy of Mn^{++} ion and CO_3^{--} ion between 18° and 25°C. is neglected, the value -52,450 may be used for the former, and from Lewis and Randall -125,760 for the latter, then ΔF°_{291} for $MnCO_3$, from the above reaction becomes, for the two sets of data, -203,160, and -202,610. Correction to 298°, in accordance with the approximate specific heats for the reaction

$$Mn(\alpha) + C(graphite) + \tfrac{3}{2} O_2 = MnCO_3,$$

$$\Delta C_p \text{ (near } 25^\circ C.) = +1.35,$$

reduces these values approximately 500 calories, so that we have $\Delta F^\circ_{298}\ (MnCO_3)$ = -202,660, and -202,110. These figures agree surprisingly well with the previous one, -200,880, obtained from the third law, especially when the many

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approximations in the calculation from solubility data are considered, as well as the possible uncertainty of at least 800 calories in the heat of formation of the carbonate.

MANGANESE SULPHATE

Although manganese sulphate occurs in several hydrated forms in nature, these materials have little significance for metallurgical purposes. The present discussion is limited to the anhydrous sulphate. The density of the anhydrous salt is probably near 3.25.

Specific Heats

No specific heats of manganous sulphate at low temperatures are available, and the entropy cannot be determined directly. The only available figure for specific heat is the very old one of Pape (287), who reported 0.182 per gram, or 27.5 per $MnSO_4$, as mean heat from 20° to 100°C. Friedrich and Blicke (99) reported that the sulphate melts at 700°C., but Hofman and Wanjukow (165) found no evidence for fusion at temperatures above 750°C. The pressure of thermal decomposition becomes an atmosphere at 1,020° - 1,030°C.

The value of 7 calories per gram-atom, which was selected as the limiting specific heat for the oxides, may be assumed to be reached at 1,027°C.

Then $$C_p(MnSO_4) = 26.6 + 1.5 \cdot 10^{-2} t,$$

$$C_p(MnSO_4) = 22.5 + 1.5 \cdot 10^{-2} T.$$

The question of possible allotropic modifications of anhydrous $MnSO_4$ is one that cannot be settled definitely by the data now available. Thus Friedrich and Blicke, studying heating curves, found arrest points at 700° and 860°C. Hofman found similar points but ascribed the effect to decomposition. In discussing the thermal decomposition of $MnSO_4$, it will be shown later than an anomalous condition prevails at 880°C.

Honda and Soné (167) made measurements of magnetic susceptibility between -200° and 1,200°C. Their data show a slight change of trend of the curve showing permeability v. temperature at slightly above 700°C. and a very marked change near 850°C.

Thermal Decomposition

By far the best data on the thermal decomposition of $MnSO_4$ are those of Marchal (241). The sulphate decomposes into a mixture of SO_2, SO_3, and O_2, with Mn_3O_4 as the solid phase. It may be supposed that the primary reaction is

$$3MnSO_4 = Mn_3O_4 + 2SO_3 + SO_2:$$

The sulphur trioxide so formed dissociates further into SO_2 and O_2, and the amounts of the various gaseous constituents may be determined if it is assumed

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that equilibrium is attained in the reaction

$$2SO_3 = 2SO_2 + O_2,$$

as well as in the primary reaction.

To calculate ΔC_p for the dissociation reaction, a special expedient must be used, because no data are available for the specific heat of SO_3. However, Lewis and Randall have shown that if ΔC_p is assumed zero for the reaction

$$2SO_3 = 2SO_2 + O_2,$$

a remarkably consistent value is obtained for the integration constant of the free-energy equation for this latter reaction. Then ΔC_p must be the same for the primary reaction as for the sum of the primary reaction and the SO_3 dissociation, that is,

$$3MnSO_4 = Mn_3O_4 + 3SO_2 + O_2.$$

Then the specific heats for this reaction are given by the following expressions:

$$C_p(Mn_3O_4) = 19.25 + 5.38\cdot10^{-2}T - 2.09\cdot10^{-5}T^2$$

$$C_p(3SO_2) = 23.10 + 1.59\cdot10^{-2}T - 0.25\cdot10^{-5}T^2$$

$$C_p(O_2) = 6.50 + 0.10\cdot10^{-2}T$$

$$\text{Sum} \quad 48.85 + 7.07\cdot10^{-2}T - 2.34\cdot10^{-5}T^2$$

$$C_p(3MnSO_4) = 667.5 + 4.50\cdot10^{-2}T$$

$$\Delta C_p = -18.65 + 2.57\cdot10^{-2}T - 2.34\cdot10^{-5}T^2$$

$$\Sigma = -R \ln K - 18.65 \ln T + 1.285\cdot10^{-2}T - 0.39\cdot10^{-5}T^2.$$

Table 52 gives the data of Marchal and the corresponding figures from which Σ is determined. Figure 11 shows the results graphically as Σ v. $\frac{1}{T}$.

Reference to the figure shows that except at the ends of the chart good concordance with the required straight line is obtained. At low temperatures the points deviate markedly, however. If a line (shown dotted) is passed through the two lowest points, it intersects the full line at a temperature of 878°, which is approximately the arrest points 850 and 860, obtained by other investigators mentioned above. The slope of the full line, that is, ΔH_o is +153,800 calories and of the dotted one 221,000. These figures may be used to calculate the heat of formation of $MnSO_4$ in order to determine the validity of the data.

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TABLE 52. - $\sum$ Function for Reaction $3MnSO_4 = Mn_3O_4 + 2SO_3 + SO_2$

or Its Equivalent, $3MnSO_4 = Mn_3O_4 + 3SO_2 + O_2$

Temperature °C.	Temperature °K.	$\frac{1}{T} \cdot 10^3$	P_{atm}	P_{SO_3}	P_{SO_2}	K	-R ln K	$\sum$
820	1,093	0.915	0.0241	0.000933	0.0175	$1.524 \cdot 10^{-8}$	35.793	-85.303
850	1,123	.8905	.0517	.00221	.0374	$1.826 \cdot 10^{-7}$	30.855	-90.621
890	1,163	.860	.1159	.00521	.0836	$2.269 \cdot 10^{-6}$	25.845	-96.122
900	1,173	.8525	.1395	.00645	.1006	$4.186 \cdot 10^{-6}$	24.626	-97.465
920	1,193	.8380	.2132	.01026	.1535	$1.615 \cdot 10^{-5}$	21.941	-100.395
930	1,203	.8315	.2278	.01054	.1641	$1.822 \cdot 10^{-5}$	21.703	-100.755
940	1,213	.8245	.2843	.01355	.2050	$3.762 \cdot 10^{-5}$	20.259	-102.321
950	1,223	.8180	.3226	.01514	.2323	$5.32 \cdot 10^{-5}$	19.570	-103.131
960	1,233	.8110	.4081	.02040	.2931	$1.221 \cdot 10^{-4}$	17.916	-104.898
970	1,243	.8045	.4474	.02146	.3220	$1.483 \cdot 10^{-4}$	17.532	-105.405
980	1,253	.7980	.5093	.02422	.3667	$2.157 \cdot 10^{-4}$	16.786	-106.262
990	1,263	.7920	.5978	.02854	.4302	$3.480 \cdot 10^{-4}$	15.835	-107.331
1,000	1,273	.7855	.6935	.03330	.4995	$5.54 \cdot 10^{-4}$	14.911	-108.376
1,020	1,293	.7733	.887	.04223	.639	$1.142 \cdot 10^{-3}$	13.472	-110.043
1,030	1,303	.7677	1.024	.04898	.738	$1.770 \cdot 10^{-3}$	12.607	-111.035
1,040	1,313	.7618	1.144	.0541	.823	$2.41 \cdot 10^{-3}$	11.987	-111.769
1,050	1,323	.7560	1.330	.0636	.957	$3.870 \cdot 10^{-3}$	11.045	-112.828
1,060	1,333	.7503	1.515	.0721	1.091	$5.67 \cdot 10^{-3}$	10.286	-113.702
1,070	1,343	.7445	1.747	.0841	1.257	$8.89 \cdot 10^{-3}$	9.391	-114.711
1,080	1,353	.7390	1.931	.0924	1.391	$1.188 \cdot 10^{-2}$	8.814	-115.404
1,090	1,363	.7338	2.297	.1123	1.654	$2.087 \cdot 10^{-2}$	7.696	-116.629
1,100	1,373	.7282	2.632	.1301	1.893	$3.209 \cdot 10^{-2}$	6.841	-117.606
1,110	1,383	.7230	3.620	.1475	2.130	$4.634 \cdot 10^{-2}$	6.108	-118.451

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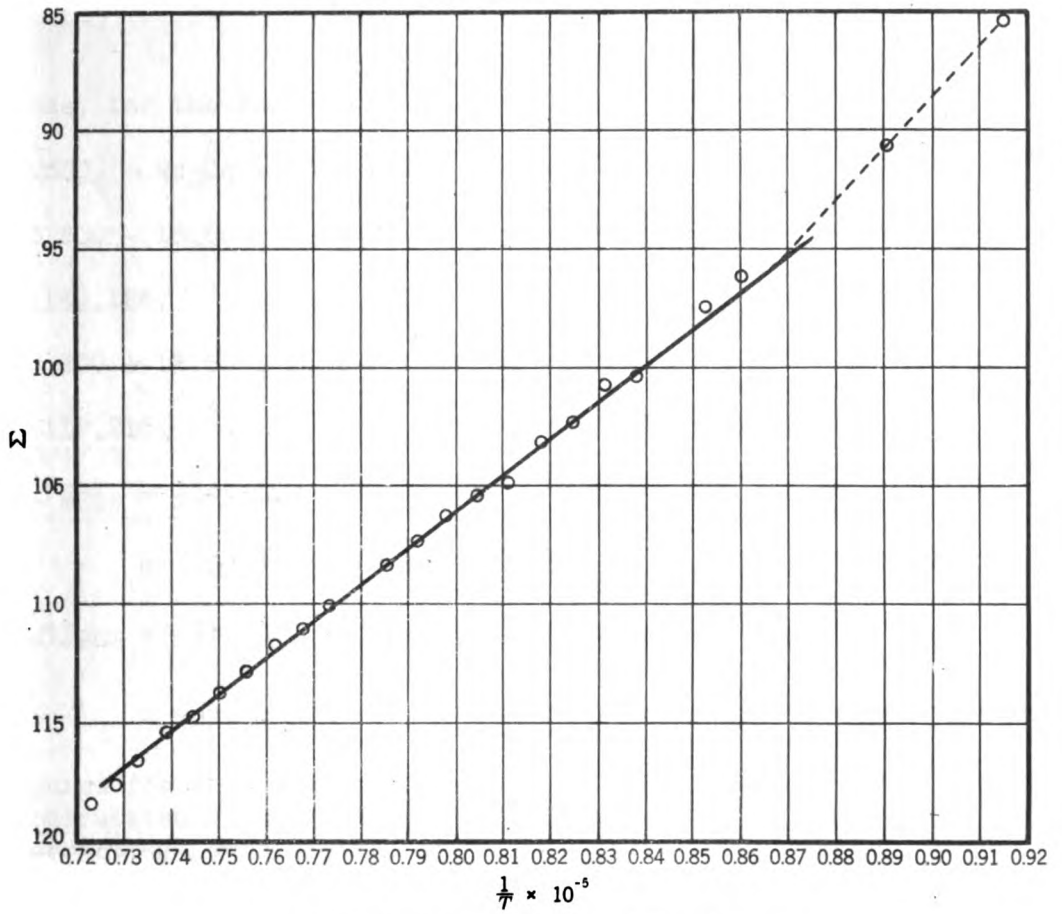

Figure 11.- Sigma function for the reaction $3MnSO_4 = Mn_3O_4 + 2SO_3 + SO_2$.

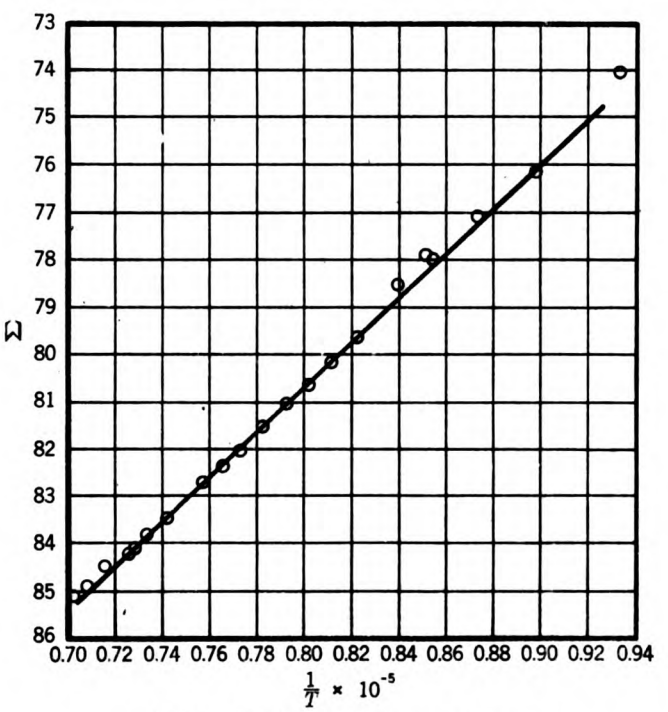

Figure 12.- Sigma function for the vaporization of $MnCl_2$.

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Thus, for the reaction

$$3MnSO_4 = Mn_3O_4 + 2SO_3 + SO_2$$

$$\Delta \underline{H}_T = 153{,}800 - 18.65\ \underline{T} + 1.285\cdot10^{-2}\underline{T}^2 - 0.78\cdot10^{-5}\underline{T}^3$$

$$\Delta \underline{H}_{298} = +149{,}186,$$

$$\Delta \underline{F}_T = 153{,}800 + 18.65\ \underline{T}\ \underline{\ln}\ \underline{T} - 1.285\cdot10^{-2}\underline{T}^2 + 0.39\cdot10^{-5}\underline{T}^3 - 229.08\ \underline{T},$$

$$\Delta \underline{F}_{298} = +117{,}210.$$

For $MnSO_4$, $\Delta \underline{H}_{298} = \dfrac{-345{,}000 + 2(93{,}540) + 70{,}940 + 149{,}186}{3},$

$$= -250{,}735$$

$$\Delta \underline{F}_{298} = \dfrac{-319{,}820 + 2(86{,}670) + 70{,}440 + 117{,}210}{3},$$

$$= -226{,}935$$

The figures for the heat and free energy of SO_2 above are taken from the recently recalculated figures of Eastman (79) and the figures for SO_3 are obtained by correcting Lewis and Randall's calculation for this material in accordance with Eastman's SO_2 revision.

Berthelot's figure for $MnSO_4$ was -249,400, which is to be compared to the calculated one of -250,735. The difference of approximately 0.4 percent is perhaps all that could be expected for this sort of calculation. The latter figure will be used for further calculations.

As final check, the entropy of $MnSO_4$ may be calculated. For the reaction

$$Mn(\alpha) + S(rh) + 2O_2 = MnSO_4$$

$\underline{S}$ 7.3 7.6 2(49.0) $\underline{x}$ $\qquad \Delta \underline{S} = \dfrac{-250{,}735 - 226{,}935}{298} = -79.8$

$$\underline{S}_{298}(MnSO_4) = \underline{x} = 33.1.$$

In the absence of any direct data, the result 33.1 for the entropy of $MnSO_4$ seems a reasonable figure.

It is evident that the slope of the dotted line will give a hypothetical value for $MnSO_4$ differing by approximately 23,000 calories from that directly determined. This difference is too great to be accounted for either by fusion or by a transition in the solid phase. It must be concluded that the upper points are in error or that a different reaction is taking place here. It seems well-proved that Mn_3O_4 is the actual product of decomposition, so that the formation of a basic salt is improbable. It can be shown that the oxygen-dissociation pressure of Mn_2O_3 at these temperatures is considerably greater than that

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from SO_3, so that the reaction here could not be the formation of this oxide. The formation of MnO_2 is even more improbable. The heat of reaction $MnSO_4 = MnO + SO_3$ is very far from the observed slope. The direction of the difference between the dotted line and the full line is such that a larger dissociation pressure would bring better concordance; and in view of this fact, the author is inclined to assume that equilibrium was not attained at the lower temperatures. These arguments may lack conviction, and it is certain that further work in this interesting problem should be done.

MANGANOUS CHLORIDE

Manganous chloride, like the sulphate, has a number of hydrated crystal forms which have little interest for the present purpose. The anhydrous material, which has been found naturally as a product of volcanic activity, has a density of approximately 3.0, and according to Sandonnini (335) melts at 650°C. The vapor density is normal.

Specific Heats

No specific heats of $MnCl_2$ at low temperatures are available, and the only determinations on this material seem to be those of Regnault (312), who reports 0.14335 for the mean specific heat per gram from 98.90 to 22.22°, and 0.14175 from 98.74 to 22.50°C. The figure 18.05 per formula weight at 60°C. will be taken as representing these results. As before, the specific heat per gram-atom will be taken as 7.0 at the melting point.

$$\text{Then } 18.05 = \underline{a} + 60\ \underline{b},$$

$$21.0 = \underline{a} + 650\ \underline{b},$$

$$\underline{b} = 5 \cdot 10^{-3},$$

$$\underline{a} = 17.75,$$

$$\underline{C_p}(MnCl_2(s)) = 17.75 + 5 \cdot 10^{-3}\underline{t},$$

$$= 16.38 + 5 \cdot 10^{-3}\underline{T}.$$

For liquid $MnCl_2$, it seems probable that the specific heat should be approximately 8 per gram atom, that is, $\underline{C_p}(MnCl_2(l)) = 24.0$. Consideration of the possible degrees of freedom of the atoms in the vapor led to the theoretical value 12. Perhaps the expression $\underline{C_p}(MnCl_2(g)) = 12 + 2 \cdot 10^{-3}\underline{T}$ will not be greatly in error.

Vapor Pressure

The only available vapor-pressure measurements on $MnCl_2$ are those of the present author (237). It seems worth while to set up a Σ-function plot for

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these results. Thus, in the reaction

$$MnCl_2(l) = MnCl_2(g),$$

$$\underline{C_p}(MnCl_2(g)) = 12.0 + 2{\cdot}10^{-3}\underline{T}$$

$$\underline{C_p}(MnCl_2(l)) = \underline{24.}$$

$$\Delta \underline{C_p} = -12 + 2{\cdot}10^{-3}\underline{T}$$

$$\Sigma = -\underline{R}\ \underline{\ln}\ \underline{p} - 12\ \underline{\ln}\ \underline{T} + 1{\cdot}10^{-3}\underline{T}.$$

The various individual figures for the Σ plot are shown in table 53, the corresponding chart in figure 12. The fact that the use of the specific heats selected above largely eliminates the curvature of the Σ v. $\frac{1}{T}$ plot compared with the log p v. $\frac{1}{T}$ curve given in the original publication confirms the order of magnitude of these assumptions. The points in the central part of the chart show an excellent conformance to the theoretical straight line, and deviations occur only in the high and low ranges, where the accuracy of the experimental method was less good.

TABLE 53. - Σ Function for Vaporization of $MnCl_2$

Temperature, °K.	$\frac{1}{T}{\cdot}10^3$	V.P.		Log V.P., atmospheres	$-R\ \ln\ p$	Σ
		Millimeters	Atmospheres			
1,071.7	0.9333	10.0	0.0131	-1.8808	8.612	-74.043
1,113.5	.8980	25.1	.0330	-1.4813	6.782	-76.290
1,145.6	.8733	33.0	.0434	-1.3624	6.238	-77.147
1,160.3	.8518	41.1	.0541	-1.2670	5.801	-77.722
1,157.1	.8542	47.2	.0621	-1.2070	5.526	-77.956
1,190.6	.8398	54.3	.0714	-1.1461	5.249	-78.553
1,215.3	.8227	83.7	.1101	-.9584	4.388	-79.630
1,232.2	.8115	102.4	.1346	-.8706	3.986	-80.184
1,246.1	.8023	121.0	.1593	-.7980	3.654	-80.637
1,261.4	.7928	138.9	.1826	-.7385	3.381	-81.042
1,278.1	.7828	168.0	.2210	-.6556	3.002	-81.547
1,293.3	.7732	201.0	.2644	-.5778	2.646	-82.029
1,305.9	.7657	226.4	.2980	-.5259	2.408	-82.384
1,320.5	.7572	251.2	.3305	-.4808	2.201	-82.714
1,347.7	.7420	330.9	.4352	-.3614	1.655	-83.460
1,363.2	.7338	374.8	.4930	-.3071	1.406	-83.832
1,372.6	.7283	410.0	.5395	-.2681	1.228	-84.094
1,378.5	.7255	426.1	.5605	-.2514	1.151	-84.204
1,398.6	.7152	455.0	.5985	-.2228	1.020	-84.489
1,412.8	.7080	529.1	.696	-.1575	.721	-84.904
1,423.3	.7025	565.5	.744	-.1288	.590	-85.110

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The slope of the Σ-function plot indicates that the heat of vaporization is

$$\underline{H}_0 = +46,950,$$

$$\underline{H}_T = 46,950 - 12\,\underline{T} - 2\cdot10^{-3}\underline{T}^2,$$

$$\underline{H}_{298} = +43,550,$$

$$\underline{F}^\circ_T = 46,950 - 12\,\underline{T}\ln\underline{T} - 1\cdot10^{-3}\underline{T}^2 - 118.27\,\underline{T},$$

$$\underline{F}^\circ_{298} = +31,972.$$

The free-energy equation above is undoubtedly better for purposes of extrapolation than the original log p v. $\frac{1}{T}$ plot in the original reference. In view of this fact, table 54 and figure 13 show the vapor pressures calculated from the equation. Using this method of extrapolation, the normal boiling point is 1,175°C., whereas the figure 1,190° was obtained by the less-accurate method of extrapolation used previously.

Thermal and Equilibrium Data

Using a dynamic method, Jellinek and Von Podjaski (179) have determined the equilibrium concentration of the gases for the reaction

$$MnCl_2(s) - H_2S = MnS - 2HCl.$$

at three different temperatures, approaching equilibrium from both sides at the intermediate point. These figures may be used to calculate the free energy of the solid chloride. Thus

$\underline{C}_p(2HCl)$	$= 13.52 + 1.212\cdot10^{-3}\underline{T} + 0.26\cdot10^{-6}\underline{T}^2$
$\underline{C}_p(MnS)$	$= 10.21 + 6.56\cdot10^{-3}\underline{T} - 2.42\cdot10^{-6}\underline{T}^2$
Sum	$23.73 + 7.77\cdot10^{-3}\underline{T} - 2.16\cdot10^{-6}\underline{T}^2$
$\underline{C}_p(H_2S)$	$= 7.20 + 3.60\cdot10^{-3}\underline{T}$
$\underline{C}_p(MnCl_2)$	$= 16.38 + 5.0\cdot10^{-3}\underline{T}$
Sum	$23.58 + 8.60\cdot10^{-3}\underline{T}$

$$\text{Difference} = \Delta\,\underline{C}_p = 0.15 - 0.83\cdot10^{-3}\underline{T} - 2.16\cdot10^{-6}\underline{T}^2$$

$$\Sigma = -R\ln K + 0.15\ln T - 0.415\cdot10^{-3}T - 0.36\cdot10^{-6}T^2.$$

The various items calculated for this latter formula are listed in table 55 and shown graphically in figure 14 as Σ v. $\frac{1}{T}$.

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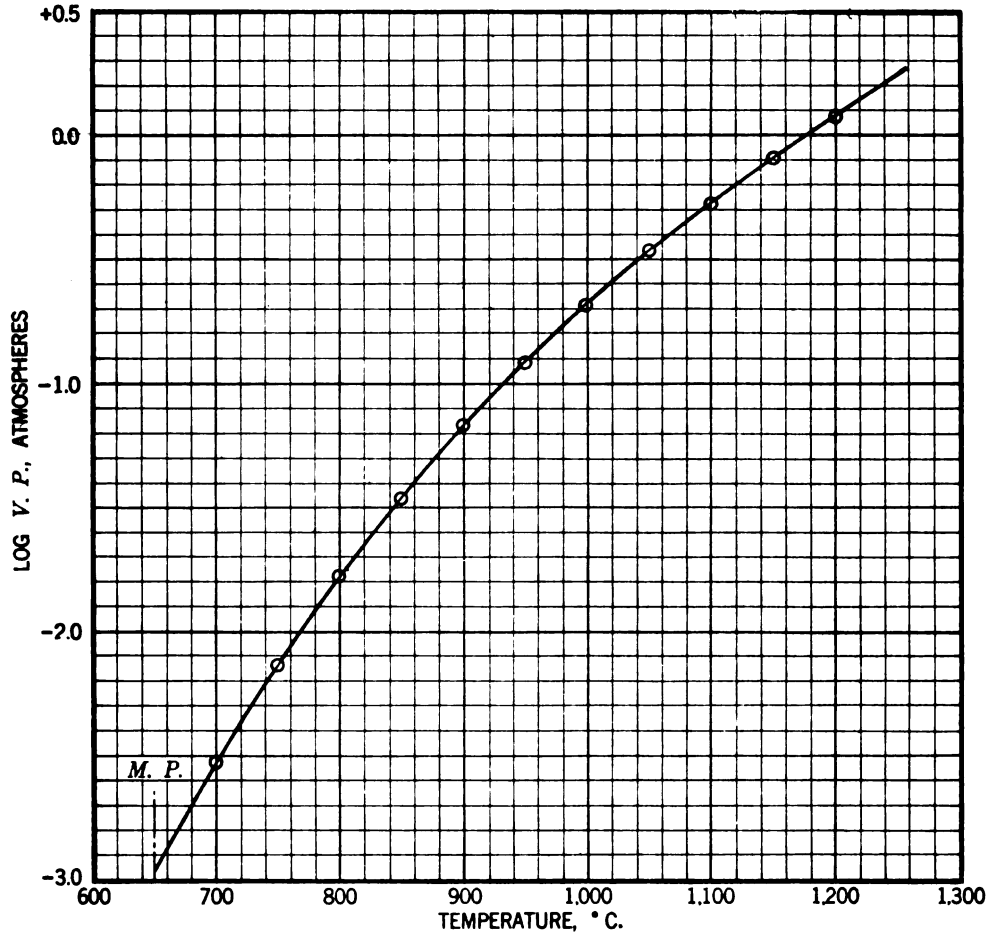

Figure 13.- Vapor pressure of $MnCl_2$.

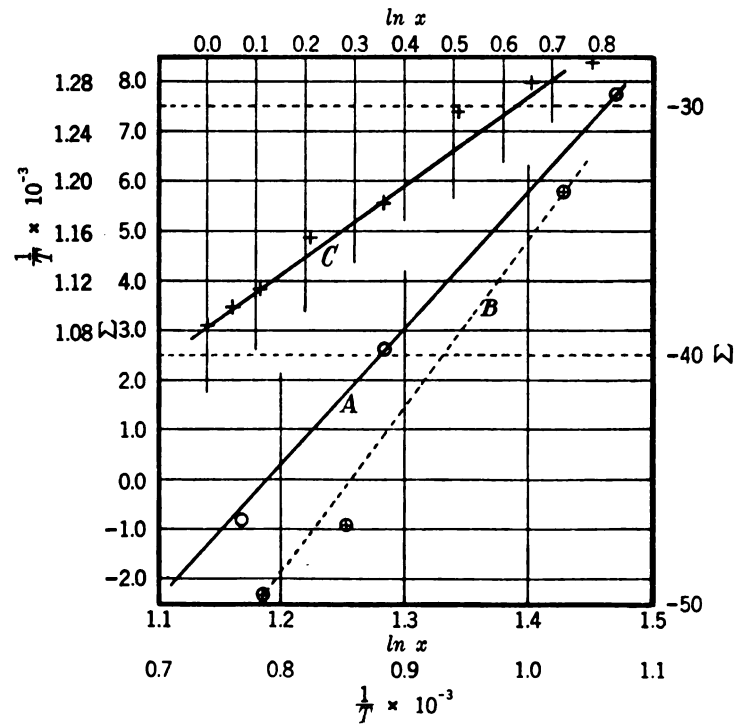

Figure 14.- Equilibrium data for $MnCl_2$: A, $MnCl_2(s) + H_2S = MnS + 2HCl$; B, $MnCl_2(l) + H_2 = Mn(s) + 2HCl$; C, $MnCl_2(s) = MnCl_2(l)$.

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TABLE 54. - Vapor Pressures of $MnCl_2$

Temperature, °C.	Log V.P., atmospheres	V.P.	
		Atmospheres	Millimeters
650.....	-2.969	$1.08 \cdot 10^{-3}$	0.8
700.....	-2.526	$2.98 \cdot 10^{-3}$	2.3
750.....	-2.133	$7.36 \cdot 10^{-3}$	5.6
800.....	-1.779	$1.67 \cdot 10^{-2}$	12.7
850.....	-1.462	$3.46 \cdot 10^{-2}$	26.3
900.....	-1.170	$6.76 \cdot 10^{-2}$	51.3
950.....	-.917	.1209	91.9
1,000.....	-.683	.2072	157.5
1,050.....	-.468	.3456	262.6
1,100.....	-.272	.5355	407.0
1,150.....	-.092	.8097	615.5
1,175.....	0	1.0	760.
1,200.....	+.073	1.182	898.

TABLE 55. - Σ Function for Reaction $MnCl_2(s) + H_2S = MnS + 2HCl$

Temperature, °C.	Temperature, °K.	$\frac{1}{T}{}^{o}K \cdot 10^3$	$K = \frac{P_{HCl}^2}{p_{H2S}}$	$-R \ln K$	Σ
407	680	1.471	0.0265	+7.220	+7.751
506	779	1.284	.335	+2.175	+2.634
583	856	1.168	1.852	-1.226	-.831

The heat of the equilibrium reaction may be determined from thermal data:

$$MnCl_2(s) + H_2S = MnS + 2HCl$$

ΔH_{298} -112,600 -4,760 -45,890 2(-22,000) ΔH = +27,470

The heats for H_2S and HCl are those used by Lewis and Randall, that for $MnCl_2$ is Berthelot's, and the MnS figure is the one selected in an earlier part of this work.

Then $\Delta H_{298} = +27,470 = \Delta H_o + 0.15\ T - 0.415 \cdot 10^{-3} T^2 - 0.72 \cdot 10^{-6} T^3$,

$\Delta H_o = +27,481.$

The middle point of the data of Jellinek and Podjaski may be selected as the most reliable, because it was approached from both sides of the equilibrium. The line shown in the chart is drawn through this point with the theoretical

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slope of $\Delta \underline{H}_0 = +27,481$. The line so drawn is almost precisely the one that might have been put through the points shown without reference to other data, and a very satisfactory interpretation of the data is thus apparent.

The heats and free energy of the reaction are then given by the expressions

$$\Delta \underline{H}_T = +27,481 + 0.15\ \underline{T} - 0.415 \cdot 10^{-3} \underline{T}^2 - 0.72 \cdot 10^{-6} \underline{T}^3,$$

$$\Delta \underline{F}^o_T = +27,481 - 0.15\ T \ln T + 0.415 \cdot 10^{-3} \underline{T}^2 + 0.36 \cdot 10^{-6} \underline{T}^3 - 32.64\ \underline{T},$$

$$\Delta \underline{F}^o_{298} = +17,538.$$

Again writing the reaction

$$MnCl_2(s) + H_2S = MnS + 2HCl.$$

$$\Delta \underline{F} \qquad \underline{x} \qquad -7,840 \quad -47,025 \quad 2(-22,692) \qquad \Delta \underline{F} = +17,538$$

$$\underline{x} = \Delta \underline{F}^o_{298}(MnCl_2(s)) = -102,107.$$

Finally, the entropy may be calculated

$$Mn(\alpha) + Cl_2 = MnCl_2,$$

$$7.3 \qquad 53.0 \qquad \underline{s} \qquad\qquad \Delta \underline{S} = \frac{-112,600 + 102,107}{298} = -35.2$$

$$\underline{S}_{298}(MnCl_2(s)) = \underline{x} = 25.1.$$

Further equilibria for the reduction of $MnCl_2$ by H_2, have been measured at higher temperatures by Jellinek and Rudat (178). These authors give three determinations of equilibrium concentrations, at 700°, 900°, and 1,000°C. It has been shown in an earlier part of this work that a transition in solid manganese probably occurs at 825°C., involving 148 calories per Mn. This small heat change is well within the uncertainty of our knowledge of the heats of formation of $MnCl_2$, and the results will be first calculated on the basis of β manganese.

The reaction on this basis is

$$MnCl_2(l) + H_2 = Mn(\beta) + 2HCl$$

$\underline{C}_p(2HCl)$	$= 13 + 2 \cdot 10^{-3} \underline{T}$
$\underline{C}_p(Mn\beta)$	$= 9$
Sum	$22.00 + 2 \cdot 10^{-3} \underline{T}$
$\underline{C}_p(H_2)$	$= 6.50 + 0.9 \cdot 10^{-3}$
$\underline{C}_p(MnCl_2(l))$	$= 24.0$
Sum	$30.50 + 0.9 \cdot 10^{-3}$
Difference $= \Delta \underline{C}_p$	$= -8.50 + 1.1 \cdot 10^{-3} \underline{T}$
Σ	$= -\underline{R} \ \underline{\ln}\ \underline{K} - 8.50\ \underline{\ln}\ \underline{T} + 0.55 \cdot 10^{-3} \underline{T}.$

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TABLE 56. - Σ Function for Reaction $MnCl_2(l) + H_2 = Mn(\beta) + 2HCl$

Temperature °C.	Temperature °K.	$\frac{1}{T} \cdot 10^3$	HCl, percent	Pressure, mm	V.P. $MnCl_2$, mm	p_{HCl}, atm	p_{H_2}, atm	$K = \frac{p^2_{HCl}}{p_{H_2}}$	$-R \ln K$	$-8.50 \ln T$	$0.55 \cdot 10^{-3} T$	Σ
700	973	1.028	0.21	760	2.3	$2.09 \cdot 10^{-3}$	0.995	$4.402 \cdot 10^{-6}$	24.525	-58.481	+0.535	-33.421
900	1,173	.8525	4.28	773	51.3	$4.06 \cdot 10^{-2}$	.909	$1.815 \cdot 10^{-3}$	12.550	-60.067	.644	-46.873
1,000	1,273	.7857	7.85	773	157.5	$6.36 \cdot 10^{-2}$	.746	$5.415 \cdot 10^{-3}$	10.379	-60.771	.700	-49.692

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The individual figures for the various components of Σ are shown in table 56 and plotted in figure 14. The values 4.28 and 7.85 differ from those given by the original authors (4.4 and 7.7), because in replotting their individual analysis at various rates of gas flow, and extrapolating to zero flow, greater weight has been given to the figures at higher velocity. There seems good reason for doing so, since at the upper temperatures the vapor pressure of $MnCl_2$ is considerable, and experimentally there seemed to be considerable chance for reversal of the equilibrium in the exit parts of the apparatus.

The points on the Σ-function plot so obtained do not lie upon a straight line, nor is there available direct evidence for the slope of the curve. The proper line may be determined if the heat of fusion of $MnCl_2$ is known. Fortunately, the heat of fusion of $MnCl_2$ may be calculated from the melting points of the $MnCl_2$ - $SrCl_2$ system investigated by Sandonnini (336). These two materials form a nearly perfect solution, with a well-defined eutectic.

For a perfect solution, the heat of fusion may be obtained from the expression

$$R \ln x = \frac{L(T_{F_o} - T_F)}{T_{F_o} T_F}$$

$$= \frac{L}{T_F} - \frac{L}{T_{F_o}},$$

where x is the mole fraction of the constituent whose pure crystals are in equilibrium with the melt, L the heat of fusion, T_{F_o} and T_F the freezing points of the pure constituent and melt, respectively. Further, if $\ln x$ is plotted against $\frac{1}{T_F}$, the slope of the line is $\frac{L}{R}$.

Table 57 shows the individual figures corresponding to the experimental points of Sandomini and figure 14 is a chart of the points as indicated above.

TABLE 57. - Melting-Point Data for System $MnCl_2$ - $SrCl_2$

Mole, percent $MnCl_2$	$\ln x$	T_F	$\frac{1}{T_F} \cdot 10^3$
100	0	923	1.084
95	0.0509	910	1.099
90	.1060	899	1.113
80	.2089	866	1.155
70	.357	846	1.182
60	.509	796	1.256
50	.693	782	1.279
46	.776	772	1.295

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Reference to the chart shows that the points in the table may fairly well be represented by a straight line with a slope corresponding to 7,110 calories.

Then for the reaction

$$MnCl_2(s) = MnCl_2(l)$$

$$\underline{C_p}(MnCl_2(l)) = 24.0$$

$$\underline{C_p}(MnCl_2(s)) = \underline{16.38 + 5.0\cdot10^{-3}\underline{T}}$$

$$\Delta \underline{C_p} = 7.62 - 5.0\cdot10^{-3}\underline{T}.$$

Furthermore,

$$\Delta \underline{H}_{923} = 7{,}110 = \Delta \underline{H}_o + 7.62\ \underline{T} - 2.5\cdot10^{-3}\underline{T}^2,$$

$$\Delta \underline{H}_o = 2{,}206,$$

$$\Delta \underline{H}_{\underline{T}} = 2{,}206 + 7.62\ \underline{T} - 2.5\cdot10^{-3}\underline{T}^2,$$

$$\Delta \underline{H}_{298} = +4{,}256.$$

Similarly,

$$\Delta \underline{F}_{923} = 0 = 2{,}206 - 7.62\ \underline{T}\ \underline{\ln}\ \underline{T} + 2.5\cdot10^{-3}\underline{T}^2 + \underline{I}\ \underline{T},$$

$$\underline{I} = +47.30,$$

$$\Delta \underline{F}^o_{\underline{T}} = 2{,}206 - 7.62\ \underline{T}\ \underline{\ln}\ \underline{T} + 2.5\cdot10^{-3}\underline{T}^2 + 47.30\ \underline{T},$$

$$\Delta \underline{F}^o_{298} = +3{,}603.$$

Referring again to the melting reaction

$$MnCl_2(s) = MnCl_2(l),$$

$$\Delta \underline{H}_{298}\quad -112{,}600 \cdot \underline{x} \qquad \Delta \underline{H} = +4{,}256$$

$$\underline{x} = \Delta \underline{H}_{298}(MnCl_2(l)) = -108{,}344,$$

$$\Delta \underline{F}_{298}\quad -102{,}107 - \underline{y} \qquad \Delta \underline{F} = +3{,}603$$

$$\underline{y} = \Delta \underline{F}^o_{298}(MnCl_2(l)) = -98{,}504.$$

Since the reduction reaction has been written to involve β manganese, the free energy and heat of this form are also needed.

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In the reaction

$$Mn(\alpha) = Mn(\beta),$$

$$\underline{C}_p(Mn\beta) = 9.00,$$

$$\underline{C}_p(Mn\alpha) = 3.78 + 7.38\cdot10^{-3}\underline{T},$$

$$\Delta\underline{C}_p = 5.22 - 7.38\cdot10^{-3}\underline{T}.$$

At the transition point, 835°C., = 1,108°K.,

$$\Delta\underline{H}_{1,108} = 148 = \Delta\underline{H}_o + 5.22\ \underline{T} - 3.69\cdot10^{-3}\underline{T}^2,$$

$$\Delta\underline{H}_o = -1,102,$$

$$\Delta\underline{H}_T = -1,102 + 5.22\ \underline{T} - 3.69\cdot10^{-3}\underline{T}^2,$$

$$\Delta\underline{H}_{298} = +126,$$

$$\Delta\underline{F}^o_{1,108} = 0 = -1,102 - 5.22\ \underline{T}\ \underline{ln}\ \underline{T} + 3.69\cdot10^{-3}\underline{T}^2 + \underline{I}\ \underline{T},$$

$$\underline{I} = +33.52,$$

$$\Delta\underline{F}^o_T = -1,102 - 5.22\ \underline{T}\ \underline{ln}\ \underline{T} + 3.69\cdot10^{-3}\underline{T}^2 + 33.52\ \underline{T},$$

$$\Delta\underline{F}^o_{298} = +456.$$

Returning now to the reduction reaction:

$$MnCl_2(l) + H_2 = Mn(\beta) + 2HCl.$$

$\Delta\underline{H}_{298}$	-108,344	0	+126	2(-22,000)	$\Delta\underline{H}$ = +64,470
$\Delta\underline{F}^o_{298}$	-98,504	0	+456	2(-22,692)	$\Delta\underline{F}$ = +53,576

$$\Delta\underline{H}_{298} = 64,470 = \Delta\underline{H}_o - 8.50\ \underline{T} + 0.55\cdot10^{-3}\underline{T}^2,$$

$$\Delta\underline{H}_o = +66,957.$$

The theoretical slope for the line of the Σ-function plot shown in figure 14, in accordance with these computations, should be $\Delta\underline{H}_o$ = +66,957. If the upper point is assumed the most accurate one (because of the low vapor pressure of $MnCl_2$) a line drawn through it with this slope strikes the lowest point very closely, but missing the intermediate one. The line so drawn is represented by the free-energy equation

$$\Delta\underline{F}^o_T = +66,957 - 8.50\ \underline{T}\ \underline{ln}\ \underline{T} - 0.55\cdot10^{-3}\underline{T}^2 - 102.22\ \underline{T},$$

the value of integration constant $\underline{I}$ = -102.22 being determined from the upper point. Whence, by calculation to 298°K., there is found $\Delta\underline{F}^o_{298}$ = +50,880.

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This value does not compare too well with the result +53,576, calculated directly from fusion data. The discrepancy cannot be due to error in the heat of fusion of manganese chloride, because even considerable changes in the value of the selected heat, if introduced into the above estimates, largely compensate, leaving the discrepancy virtually unchanged. Moreover, equilibrium and thermal data are so well in accord for the previously calculated reaction between the chloride and hydrogen sulphide, that error in the solid $MnCl_2$ results hardly seems probable. It seems more probable to suppose that the relatively great vapor pressure of $MnCl_2$ caused experimental errors (perhaps due to reversal of the reaction on cooling the gaseous products). On this basis, the figures for liquid $MnCl_2$ will be taken from those calculated from the solid, and the melting reaction.

The measurements of the decomposition voltage of $MnCl_2$ by Devoto and Guzzi (69) are obviously unsuited to calculation of free energy of fused $MnCl_2$, as the authors themselves showed from related data.

MANGANESE CARBIDE

In spite of the technical importance of manganese carbide, there are few investigations on record furnishing thermodynamically useful data. According to Stadeler (353), carbon forms with manganese the compound Mn_3C, melting at 1,217°C. and with a density of 6.9. Stadeler's melting-point determinations show mutual solubility, with a maximum in the melting curve at 3 percent carbon (Mn_3C = 6.8 percent) and at 1,270°C. The correct melting point of pure manganese has been taken in this work at 1,220°C., whereas Stadeler gave 1,207.

Other melting points for this composition of carbide are given by Ruff and Gersten (329), who found 1,243° as the mean of three determinations, and by Heraeus (148) at 1,245°C.

The manganese metal used by Stadeler analyzed only 95.8 percent manganese, and contained more than 1 percent each iron, aluminum, and silicon. The finality of measurements on so impure a material may be questioned, and it is not impossible that the melting diagram carried out with pure manganese might not show the maximum observed. It is probable, however, that the mixed crystals revealed by Stadeler's work are well-authenticated.

The carburization of manganese with methane was studied by Hilpert and Paunescu (163). Upon passing a mixture of equal parts of methane and hydrogen over electrolytically prepared manganese for long periods of time (45 hours), these investigators found the following limiting values of carbon content were reached: 600°C., 5.7 percent C; 700°, 8.6 percent C; 800°, 13.5 percent C; 900°, 15 percent C. One must conclude from these experiments either that carbides of higher carbon content than Mn_3C are capable of forming or that the analyses made included elementary carbon from the thermal decomposition of methane. The authors took precautions, however, to remove elementary carbon, and the former alternative seems preferable. It will be necessary to return to these data later.

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The solubility of carbon in liquid manganese has been measured by Ruff and Bormann (328), who found 6.82 percent C at 1,312°, 6.93 percent at 1,427°, 7.05 percent at 1,492°, and 7.12 percent at 1,525°. These authors also determined that the latter solution boiled under 30 mm pressure at 1,526°C., and upon heating further they determined that the vapor contained 1.94 percent C, the maximum temperature used being near 2,000° - 2,100°C. Pure manganese boils at 30 mm pressure at 1,511°C., and the low percentage of carbon in the vapor shows that the gas is mostly uncombined manganese. Then the liquid must have a relatively high concentration of free manganese. If the vapor pressure of the carbide at 1,526° is neglected, one may calculate the mole fraction of manganese in the liquid from Raoult's law. By interpolation in table 46 (p.106), the vapor pressure of pure manganese at 1,526°C. is 33.35 mm, whence the mole fraction of manganese is $\frac{30}{33.35} = 0.899$, yet the melt contains slightly more than enough carbon to convert all the manganese to Mn_3C and is saturated with carbon, since the experiments were performed in graphite crucibles.

It is not allowable, however, to assume that the carbon is present in solution as such, for then the mole fraction of manganese would be

$$\left(\frac{100 - 7.12}{55}\right) \div \left(\frac{100 - 7.12}{55} + \frac{7.12}{12}\right) = 0.74,$$

and a much greater raising of the boiling point would ensue. The accuracy of Ruff and Bormann's boiling-point determinations is well attested by the calculations from spectroscopic data made in an early part of this work, and one must assume that the figure 0.899 is quite precise.

In seeking explanation for this anomalous condition, one may assume other carbides, or mixtures of carbides and carbon, to be present. Thus assuming two unknown proportions, say x and y, of any two constituents, simultaneous expressions may be set up, one showing the mole fraction of manganese and the other the total carbon content, both of these quantities being known and fixed. The solution of these equations for Mn_2C and Mn_3C, Mn_2C and C, MnC and Mn_3C, MnC and C, MnC_2 and Mn_3C, MnC_2 and C, all lead to impossible values, either x or y being negative. It is, moreover, apparent from the quantities involved that the carbide must have a relatively high molecular weight to permit a possible and necessary 0.899 mole fraction of pure manganese to exist.

By analogy with the oxide, one may finally try Mn_3C_4 as the molecular species involved. The ratio

$$\frac{Mn_3C_4}{4C} = \frac{212.8}{48} = 4.429,$$

then 7.12 percent carbon corresponds to 7.12 x 4.429 = 31.55 percent Mn_3C_4, and the mole fraction of manganese is

$$\left(\frac{100 - 31.55}{55}\right) \div \left(\frac{100 - 31.55}{55} + \frac{31.55}{212.8}\right) = 0.894.$$

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This is too close concordance with the 0.899 calculated from Raoult's law to be a mere coincidence. The conclusion seems justified, then, that the carbide in solution is Mn_3C_4.

In the vapor phase, however, it seems doubtful whether such a complex molecule as Mn_3C_4 can be used to explain the volatility of carbon. The carbide in the vapor state is more probably Mn_3C. Thus, if one calculates the mole fraction of manganese in the vapor state (1.94 percent C) there is obtained:

$$\text{Mole fraction Manganese} = \frac{\left(100 - \frac{1.94}{6.78}\cdot 100\right)}{\left(\frac{}{55}\right)} \div \left(\frac{100 - \frac{1.94}{6.78}\cdot 100}{55} + \frac{\frac{1.94}{6.78}\cdot 100}{177}\right) = 0.890$$

Here again the concordance with the previously calculated figures is gratifying. The reason why the mole fraction so calculated from vapor formed over a 500° temperature range is so close to that calculated for the liquid will be apparent from subsequent calculations.

If the above reasoning is accepted, the solubility of carbon measured by Ruff and Bormann represents the equilibrium

$$3Mn(l) + 4C = Mn_3C_4 \text{ (in solution)},$$

and the equilibrium constant is

$$\underline{K} = \frac{\underline{A}_{Mn_3C_4}}{\underline{A}_C^4 \cdot \underline{A}_{Mn}^3},$$

and the activity of Mn_3C_4 and liquid Mn may be taken as the mole fraction of each. Since the experiments were performed in contact with graphite as a solid phase, the activity of the carbon is unity and

$$\underline{K} = \frac{\text{m.f.}_{Mn_3C_4}}{\text{m.f.}^3_{Mn}}.$$

No specific heats for the above reaction are available, and one can only assume that $\Delta \underline{C}_p = 0$, and consequently chart log $\underline{K}$ v. $\frac{1}{T}$. The data for such calculation and plot are shown in table 58, and the points themselves in figure 15.

TABLE 58. - Solubility of C in Mn(l)

Temperature, °C.	Temperature, °K.	$\frac{1}{T}\cdot 10^3$	C, percent	m.f. Mn_3C_4	m.f. Mn	$\underline{K}$	log $\underline{K}$
1,312	1,585	0.631	6.82	0.1009	0.8991	0.1388	-0.8609
1,427	1,700	.588	6.93	.1026	.8974	.1420	-.8479
1,492	1,765	.567	7.05	.1050	.8950	.1465	-.8342
1,525	1,798	.556	7.12	.1064	.8936	.1491	-.8265

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It is apparent that the mole fraction of manganese changes very slowly with the temperature, and this may account for the possibility of calculating this quantity from analysis of the vapor, as was done previously.

All but the point at lowest temperature correspond to a satisfactory straight line with slope of $\Delta \underline{H} = +5{,}090$ calories.

Further, $\Delta \underline{F}_{1,798} = -\underline{R}\ \underline{T}\ \underline{\ln}\ \underline{K} = -4.578 \cdot 1{,}798 \cdot (-0.8265)$,

$$= +6{,}800.$$

Then, for the reaction above,

$$\Delta \underline{F}^{o}_{T} = +3{,}090 + 2.062\ \underline{T},$$

$$\Delta \underline{F}^{o}_{298} = 3{,}705.$$

Returning now to the experiments of Hilpert and Paunescu, the assumption may be made without inconsistency that the reaction occurring was

$$3Mn(s) + 4CH_4 = Mn_3C_4\,(\text{solid sol. or mixed crystals}) + 8H_2,$$

for which the formal equilibrium constant is

$$\underline{K} = \frac{\underline{A}_{Mn_3C_4}}{\underline{A}^{3}_{Mn}} \cdot \frac{\underline{A}^{8}_{H2}}{\underline{A}^{4}_{CH_4}}.$$

Here again the further assumption may be made that the activities of Mn_3C_4 and Mn are given by the respective mole fractions. Experimentally the pressures of hydrogen and methane are fixed by the equal volume mixture used in the tests. Then

$$\underline{K} = \frac{\text{m.f.}_{Mn_3C_4}}{\text{m.f.}^{3}_{Mn}} \cdot \frac{0.5^{8}}{0.5^{4}} = \frac{\text{m.f.}_{Mn_3C_4}}{\text{m.f.}^{3}_{Mn}} \cdot 0.0625.$$

Table 59 shows the figures calculated from Hilpert and Paunescu's data, and figure 15 is the plot of log $\underline{K}$ v. $\frac{1}{\underline{T}}$.

TABLE 59. - Formation of Solid Manganese Carbide

Temperature, °C.	Temperature, °K.	$\frac{1}{T} \cdot 10^3$	Carbon, percent	m.f. Mn_3C_4	m.f. Mn	$\underline{K}$	log $\underline{K}$
600	873	1.146	5.7	0.2523	0.7477	0.0378	-1.422
700	973	1.028	8.6	.3810	.6190	.1005	-.998
800	1,073	.932	13.5	.598	.402	.575	-.241
900	1,173	.853	15.0	.664	.336	1.095	+.049

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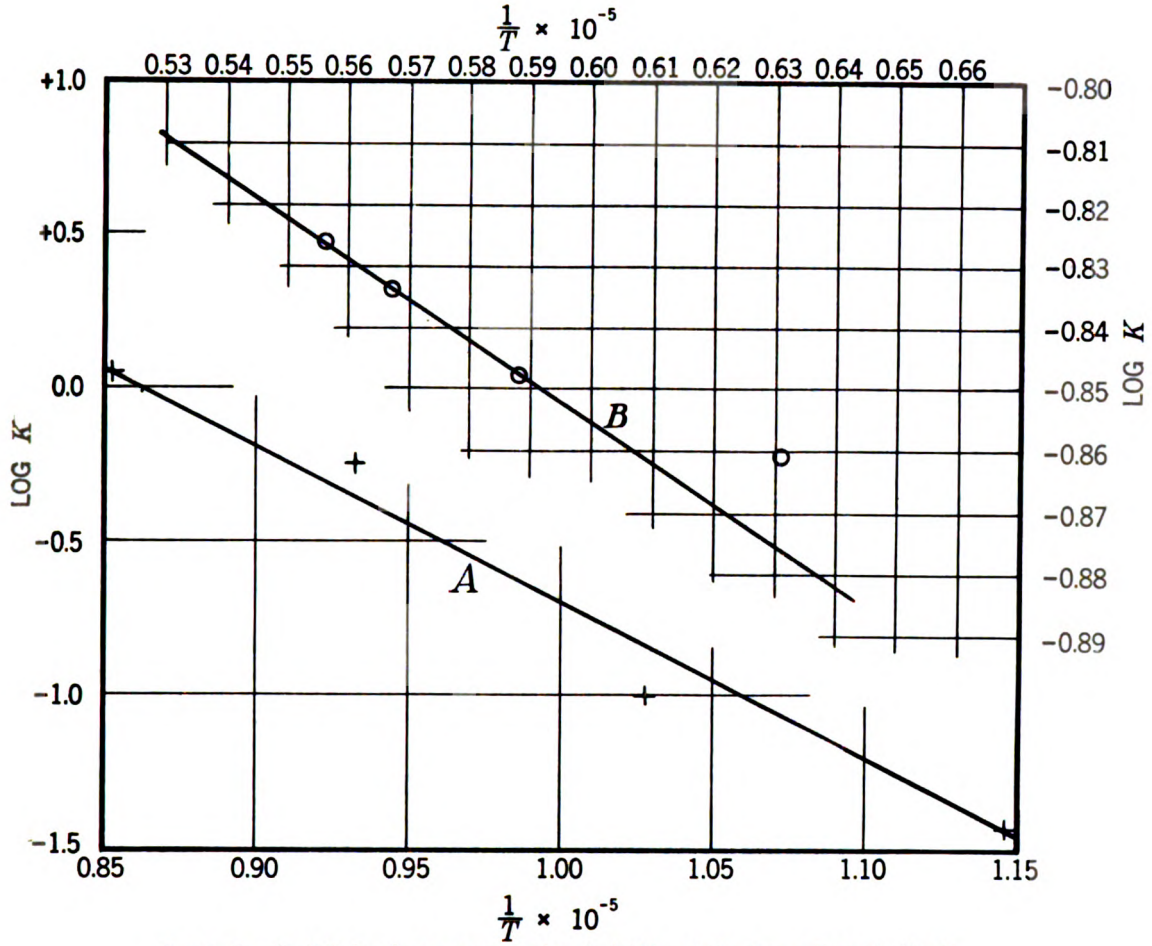

Figure 15.- Equilibria of manganese carbide: A, Solid carbide, from methane; B, liquid solution.

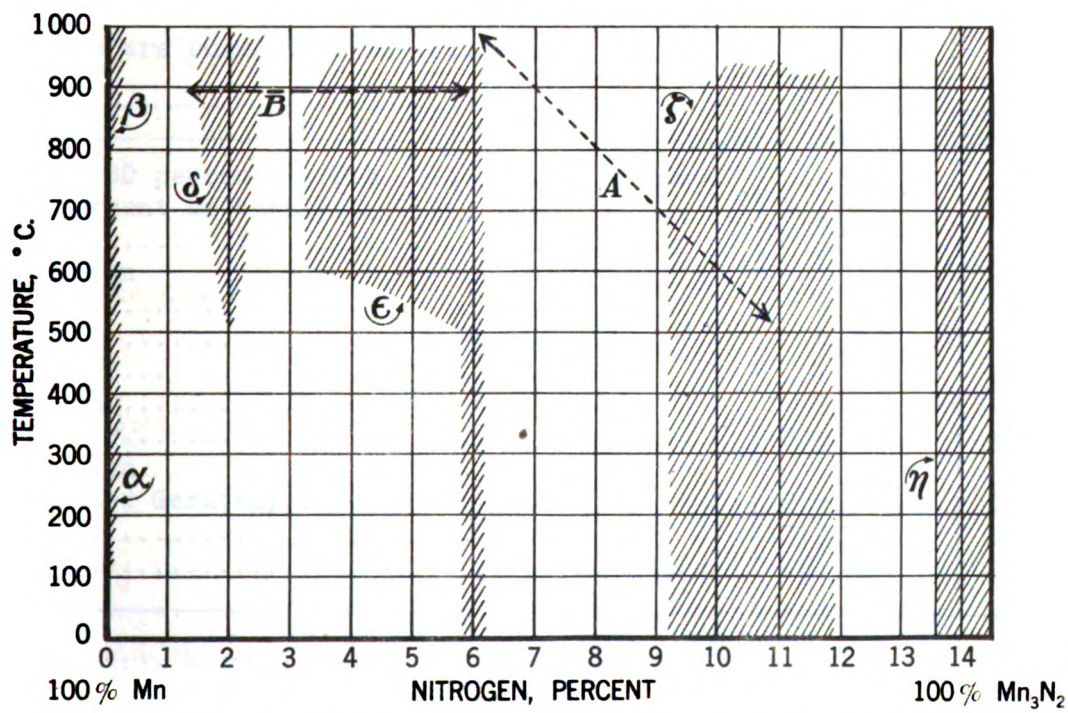

Figure 16.- Phase diagram for manganese nitrides, after Haag: A, Valenski's range; B, Tschischewsky's range.

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Figure 20 shows that a fair approximation to a straight line is indicated by these points. Too great accuracy cannot be expected, since the values of final carbon content were taken from curves in the original article, and the great number of molecules involved in the formal equilibrium expression renders the calculation very sensitive to slight errors of composition of either the solid or gaseous phase.

From the slope of the line, the heat of reaction is found to be $\Delta \underline{H}$ = +19,700 calories.

The heat of formation of methane at ordinary temperatures is $\Delta \underline{H}$ = -18,120, whence the heat of formation of Mn_3C_4 in solid solution becomes

$$\Delta \underline{H} = -52,780, \text{ and } \Delta \underline{F}_{873} = +5,680,$$

$$\Delta \underline{F}^{o}_{\underline{T}} = -52,780 + 67.00\ \underline{T},$$

$$\Delta \underline{F}^{o}_{298} = -32,810.$$

Recent direct calorimetric determinations of the heat of formation of manganese carbide are those of Roth (319) and of Ruff and Gersten (329). The former author gives $\Delta \underline{H}$ = -23,000 for Mn_3C, and recalculates Ruff and Gersten's data (for corresponding heat of formation of Mn_3C_4) to $\Delta \underline{H}$ = -27,000 calories. Roth does not give enough data in his article to permit recalculation of his results to correspond to Mn_3C_4, but it is possible to do so with the figures of Ruff and Gersten.

These data are summarized as follows:

	No. 1	No. 2
Carbide with 6.80 percent carbon.....Grams	1.6474	1.3154
Mn_3C_4 (30.1 percent of total)..... do	.4960	.3961
Free manganese..... do	1.1514	0.9193
Heat of oxidation		
Total.....	3,782	3,070
Mn.....	2,301	1,834
Mn_3C_4.....	1,481	1,236
Mn_3C_4 per gram.....	2,988	3,120
Mn_3C_4 per mole.....	635,000	664,000
Heat of formation		
Mn_3O_4 (Ruff and Gersten).....	329,000	329,000
$4CO_2$.....	379,000	379,000
Mn_3C_4.....$\Delta \underline{H}$ =	-63,000	-34,000

If the carbide truly is Mn_3C_4, accurate results of calorimetric experiments on samples containing only 30 percent of the true carbide could scarcely be expected. The order of mangitude is nearly the same as that obtained from the experiments of Hilpert and Paunescu.

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The calculations which have been made above seem to bring a fair degree of concordance to the available data, but in one respect they are still unsatisfactory. This is illustrated by the following sequence of reactions:

$$3Mn(l) + 4C = Mn_3C_4(\text{liquid sol.}) \qquad \Delta H = +3,090$$

$$3Mn(\text{solid}) = 3Mn(l) \qquad \Delta H = +11,934$$

$$3Mn(\text{solid}) + 4C = Mn_3C_4(\text{liquid sol.}) \qquad \Delta H = +15,024$$

$$Mn_3C_4(\text{solid sol.}) + 8H_2 = 3Mn(s) + 4CH_4 \qquad \Delta H = -19,700$$

$$Mn_3C_4(\text{solid sol.}) + 4C_2 + 8H_2 = Mn_3C_4(\text{liquid sol.}) + 4CH_4 \qquad \Delta H = -4,676$$

$$4CH_4 = 4C + 8H_2 \qquad \Delta H = +72,480$$

$$Mn_3C_4\ (\text{solid sol.}) = Mn_3C_4\ (\text{liquid sol.}) \qquad \Delta H = +67,804$$

It does not seem probable that the apparent heat of fusion of Mn_3C_4 calculated in this way can be as high as indicated, but it is perhaps possible.

Obviously a more satisfactory experimental investigation of the carbides of manganese must be made before any great reliance may be placed on the thermodynamic properties. It may, however, be stated that the free-energy expressions given represent the only experimental data available.

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MANGANESE NITRIDE

Elementary manganese readily absorbs gaseous nitrogen at elevated temperatures, and a number of investigations of this phenomenon have been made. Two nitrides are reported in the literature based on chemical data, Mn_5N_2, and Mn_3N_2, but a phase study of the systems involved leads to complicated and to some extent indefinite results, with the presumption of the compound Mn_4N. The data of Tschischewsky reported by Mellor (253) (original data not available) (254) show conclusive chemical evidence for the formation of the nitride Mn_3N_2, when ammonia is used for nitriding between 600° and 800° C. The calculations below show that most of the quantitative data may be explained upon the assumption that only one nitride, Mn_3N_2, is formed.

The phase changes in the Mn - N system are very important, and it is fortunate that careful X-ray studies of this system have been made by Haag (136). This author shows six distinct phases, and their disposition is best illustrated by a temperature-composition diagram, such as figure 16, which is a sketch reproduction of Haag's original.

Only for the η phase was this investigator able to assign definite positions to nitrogen and manganese atoms, and since above 500° C. this phase covers a considerable range of composition, the conclusion seems inescapable that the η phase consists of mixed crystals. The β phase, representing many of the compositions obtained by the action of nitrogen gas on metallic manganese, has, according to the author, the nitrogen atoms in den Hohlraum willkürend eingelegen, and it may therefore be considered a solid solution, with the nitride having amorphous properties; in contrast to the crystalline η phase. Although the lower composition limit corresponds to Mn_5N_2, it will be shown that the chemical properties are explained only by the assumption of Mn_3N_2 in lowered activity.

The most careful equilibria determinations between manganese, its nitrides, and nitrogen have been made by Valenski (377), who also reports the results of the experiments of Shukow (Zhukov, Yukoff, Jukow seem to be other references to the same work), whose original publication was inaccessible to the present author. Other authors who have also experimented in this field are Duparc, Wenger, and Cimerman (76, 77).

Although this considerable accumulation of data exists, unfortunately only parts of the material is usable. Thus these last authors not only had quite impure manganese metal to work with. but also the time periods used by them lead to the presumption that equilibrium was probably not attained in the solid constituents. Thus Haag found it necessary to "homogenize" his samples by long-continued heat treatment; but some of the other experimenters, such as Duparc and coworkers, have used only 1-hour treatments. Valenski, on the other hand, shows curves extending to 30 hours or more, and with nitrogen contents which have become constant in magnitude, and it may be presumed that his results probably represent truly homogeneous solid phases.

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The calculations which will be made are on the assumption that the nitriding reaction is

$$3Mn(s) + N_2 = Mn_3N_2 \text{ (solid solution or mixed crystals)},$$

$$K = \frac{A_{Mn_3N_2}}{A_{N_2} \cdot A_{Mn}^3}$$

Selecting experiments where the pressure of nitrogen was 1 atmosphere, one may write

$$K = \frac{\text{m.f.}_{(Mn_3N_2}}{\text{m.f.}^3_{(Mn)}},$$

where the activities have been replaced by the corresponding mole fractions.

The significant data, obtained under conditions seeming to insure homogeneity of the solid phase, are recorded in table 60, and plotted on the conventional log K v. $\frac{1}{T}$ chart in figure 17. The points so plotted fall upon two straight lines for the solid material, with a single point representing the liquid phase. That the intersection of these lines should be so close to the upper limit of Haag's η phase, as indicated by the dotted line, must be more than a coincidence. It seems then that the upper line represents amorphous solid solutions, its lower continuation mixed crystals, but that the chemical behavior of each is adequately explained by the single assumption of Mn_3N_2 as the nitride phase.

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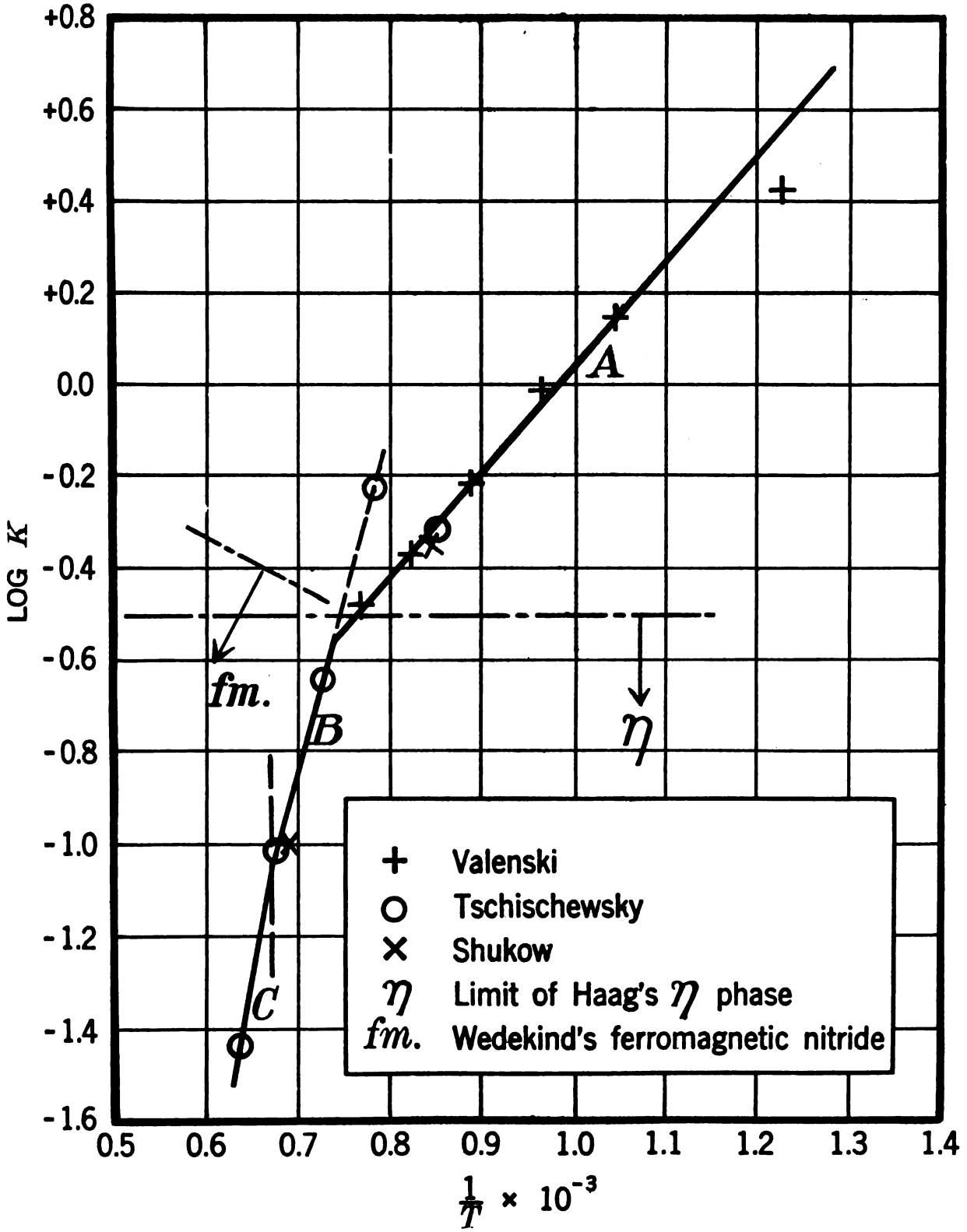

Figure 17.- Equilibrium data for manganese nitrides: A, Amorphous solid solution; B, mixed crystals; C, liquid.

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TABLE 60. - Nitriding of Manganese

Experimenter	Temperature		$\frac{1}{T} \cdot 10^3$	N, percent	Mn_3N_2 percent	m.f.		K	log K
	°C	°K				Mn_2N_3	Mn		
Valenski	540	813	1.230	10.73	74.0	0.448	0.552	2.66	0.425
	680	953	1.049	9.66	66.6	.362	.638	1.394	.144
	760	1033	.968	8.93	61.5	.313	.687	.965	- .016
	850	1123	.891	7.92	54.6	.255	.745	.616	- .211
	940	1213	.825	7.02	48.4	.211	.789	.430	- .366
	1030	1303	.767	6.37	43.9	.182	.818	.332	- .479
Tschischewsky[1]	900	1173	.852	7.3	50.3	.224	.776	.479	- .320
	1000	1273	.785	7.8	53.8	.250	.750	.593	- .227
	1100	1373	.728	5.23	36.1	.139	.861	.218	- .642
	1200	1473	.678	3.29	22.7	.077	.923	.098	-1.012
	1300	1573	.636	1.55	10.7	.033	.967	.037	-1.438
Shukow[2]	910	1183	.846	7.16	49.3	.217	.783	.445	- .352
	1175	1448	.691	3.28	22.6	.077	.923	.102	- .992

1 Omitting low temperatures. 2. 1 atmosphere.

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From the slopes of the lines and a point on each curve, the following free-energy equations may be deduced:

$3Mn(s) + N_2 = Mn_3N_2$ (amorph. solid solution),

$\Delta H = -10,300,$

$\Delta F_{1,213} = -4.578 \cdot 1,213 \cdot (-0.316)$

$= +2,030 = -10,300 + I \cdot 1,213,$

$I = +10.16,$

$\Delta F^{o}_{T} = -10,300 + 10.16\ T,$

$\Delta F^{o}_{298} = -7,270.$

Further, $3Mn(s) + N_2 = Mn_3N_2$ (mixed crystals),

$\Delta H = -33,460,$

$\Delta F_{1,373} = -4.578 \cdot 1373 \cdot (-0.642),$

$= +4,035 = -33,460 + I \cdot 1373,$

$I = -27.32,$

$\Delta F^{o}_{T} = -33,460 + 27.32\ T,$

$\Delta F^{o}_{298} = -25,315.$

And finally, $3Mn(l) + N_2 = Mn_3N_2$ (dissolved),

$\Delta F_{1,573} = -4.578 \cdot 1,573 - 1.438,$

$= +10,350 = -45,800 + I \cdot 1,573,$

$I = +35.70,$

$\Delta F^{o}_{T} = -45,800 + 35.70\ T,$

$\Delta F^{o}_{298} = -35,160.$

From the first and second reactions above the heat of crystallization may be calculated

Mn_3N_2(amorph. solid solution) = Mn_3N_2 (mixed crystals),

$\Delta H = -23,160,$

$\Delta F^{o}_{T} = -23,160 + 17.16\ T,$

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and further from the second and third reactions the heat of fusion is calculated to be ΔH = +12,340. This may be compared with the heat of fusion of 3 gram-atoms of manganese metal = 3 x 3,576 = 10,728. The former figure is composite, since the system contains both manganese and its nitride and should presumably be somewhat greater than the heat of fusion of the manganese metal only. The order of magnitude may be taken as confirmatory.

Direct determinations of the heat of formation of manganese nitride have been made by Neumann, Kruger, and Haebeler (272). These authors made direct determinations of the heat evolved by the nitriding of manganese in a bomb and indirectly by the oxidation of an externally prepared nitride sample. They assume Mn_5N_2 to be formed, largely because they obtained about 8 percent nitrogen in the first experiments. The value given is

$$\Delta H = -57,180 \pm 400 \text{ for the reaction } 5Mn + N_2 = Mn_5N_2.$$

These results are based upon a difference method, where the calorimetric ΔT for the reaction was approximately 0.05°, for a determined rise of 1.25°C., calculated by difference. Under these circumstances, it is difficult to see how any precision could have been obtained. Moreover, the phase changes disclosed by Haag's diagram lead to the supposition that their product was of indefinite composition.

In the oxidation experiments, the authors seem to have made a serious error. Their manganese was prepared by distillation of electrolytically prepared amalgam in hydrogen, and analyzed 99.75 percent manganese. They state the remainder to be nearly all hydrogen, but they do not correct (so far as their data show) for the heat evolved by oxidation of this hydrogen. Thus, they had the heat of oxidation of 1 gram of metal = 1,845.4 calories, and for a corresponding amount of nitride (5.1 percent N) 1725.5 calories. One gram of metal would contain 0.0025 gram H_2; 2 grams of hydrogen produce 57,820 calories when burned to water vapor at 25°C., then the heat of 0.0025 gram = $\frac{0.0025}{2}$ 0.57820 = 72.3 calories. Then 0.9975 gram of Mn produces 1,845.4 - 72.3 = 1,773.1 calories, or 1,777.5 per gram. One gram of Mn corresponds to 0.0537 gram of N_2, whence the heat of nitriding is

$$\frac{1775.5 - 1725.5}{0.0537} \cdot 28 = 26,100,$$

instead of the 62,400 calories per mole calculated by the authors. This figure is at least the same order of magnitude as the 33,460 calories calculated for mixed crystals. Since this sample was prepared separately at 600° - 700°C., from the bomb experiments it may be assumed that it was essentially homogeneous, and it falls well within the limits of Haag's η phase.

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The ferromagnetic properties of manganese nitride have caused considerable interest. It is worthy of note that Wedekind (380) has given the limits of preparation of the ferromagnetic material as over 1,200°C., and corresponding to 6.8 percent N. If this point is placed on the log $\underline{K}$ v. $\frac{1}{T}$ chart, it appears that the ferromagnetic field corresponds to the true mixed crystals or the γ phase of Haag and furnishes final confirmation of the point of view adopted.

The data of Duparc have not been shown on the chart, but they approach asymptotically to the lines given and are obviously results not obtained at equilibrium because of the short time periods used.

Explanation of the various data presented above has but one serious flaw; it does not include experiments which have been made at various pressures. Instead of $\underline{K}$ varying inversely as the first power of the nitrogen pressure, the data available (Shukow and Duparc) indicate that $\underline{K}$ seems to be a function of the square or cube root of the N_2 pressure. Since one cannot be certain that equilibrium in the solid phase had been obtained, it may be supposed that the pressure experiments were not, in fact, correct, and that more precise results might corroborate the assumptions made.

The variation of solubility of gas in metal according to a square- or cube-root equation has recently been discussed by Gottschalk and Dean (121). It should be noted in connection with the manganese nitride that the chemical-compound relationships seem now fairly clear, but that the pressure effect may be explained if only associated molecules react; and not dissociated molecules or atoms, as some authors suppose.

CONCLUSION

For the convenience of the user of the data which have been collected in this chapter, the figures for specific heats, free energies, entropies, and heats of formation used or found have been summarized tables 61 to 64. Before such figures are used for important calculations, reference should be made to the original calculations to indicate the limitations of the available data and in consequence of the derived free-energy expressions.

It should not be forgotten, in this connection, that the calculation of equilibria from free-energy data suffers from a considerable increase in percentage error when the resultant free energy must be obtained by the summation or difference of large individual quantities. Under such circumstances, errors of several hundred percent are possible, and the calculations may not give more than the order of magnitude of the true result. It is perhaps a surprising and reassuring circumstance that the degree of correlation obtained in the calculations is as good as indicated. The calculations seem to have brought the manganese systems to such a state that a few well-performed crucial experiments would authenticate the entire list of properties.

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Referring more specifically to the tables, the reader will note that most of the figures in table 61, showing the specific heat values used in this work, are estimated from data near room temperature. Where a third coefficient is given, it must not be forgotten that the quadratic form used, $C_p = a + bT + cT^2$, must necessarily have a maximum or minimum at some temperature specified by the relationship

$$\frac{dC_p}{dT} = 0 = b + 2cT,$$

$$T_{max} = \frac{b}{-2c}$$

It is practically certain that true specific heat values do not actually show such maximum points, and the quadratic form of expression is only even approximately correct when T_{max} falls outside of the range of validity of the expression. These maxima occur for the various materials at the following approximate temperatures: MnO, 1,150°C; Mn_2O_3, 750°; Mn_3O_4, 1,000°; MnO_2, 500°; MnS, 1,100°; $MnCO_3$, 2,100°. For the first five materials above the criterion is not satisfied, and the formulas given must not be supposed actually to represent true specific heats. The best that can be said for them is that they represent an attempt to estimate such values in the complete absence of data at high temperatures in a manner that leaves the limiting values consistent with available information.

The real difficulty here is obviously the unsuitability of the quadratic form. Unfortunately, no better substitute in the form of other analytic expressions has so far been devised.[5] Had one actual data, a preferable method of calculation would be a tabular method similar to that used for the volatilization of manganese.

In the remaining tables of free energies, entropies, etc., some attempt has been made to estimate the apparent uncertainty of the figures. Especially as regards free-energy values, these estimates are based on the writer's judgment and prejudices. It is hoped that the latter have been on the conservative side, but here again it must be pointed out that all that is claimed is that the figures given usually fit the actual available data in the range where the results are supposed to be valid. In the case of the dissociation of oxides, even this last criterion is not fulfilled, other estimates, such as the entropy of Mn_2O_3, requiring some violence to actual dissociation figures.

5 Since this was written the author, with K. K. Kelley, devised a superior form of analytical expression, which appeared in an article entitled "An Equation for the Representation of High-Temperature Heat Control", in the Journal of the American Chemical Society, Vol. 54, 1932, P. 3243.

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TABLE 61. - Summary of Specific-Heat Values Used in this Work

$(C_p = a + bT = cT^2)$

Material	Form	a	b	c	Apparent valid temperature range, °C.
Mn	α	3.78	$7.38 \cdot 10^{-3}$		0 - 835
Do	β	9.00			835 - 1,044
Do	γ	10.00			1,044 - 1,220
Do	Liquid	11.30			1,220 - 1,400
MnO[a]	Solid	7.43	$1.038 \cdot 10^{-2}$	$-3.62 \cdot 10^{-6}$	0 - 1,650
Mn_2O_3[a]	do	10.33	$5.3 \cdot 10^{-2}$	$-2.57 \cdot 10^{-5}$	0 - 1,100
Mn_3O_4[a]	do	19.25	$5.38 \cdot 10^{-2}$	$-2.09 \cdot 10^{-5}$	0 - 1,500
MnO_2[a]	do	1.92	$4.71 \cdot 10^{-2}$	$-2.97 \cdot 10^{-5}$	0 - 500
MnS[a]	do	10.21	$6.56 \cdot 10^{-3}$	$-2.42 \cdot 10^{-6}$	0 - 1,610
Do[a]	Liquid	16.			1,610 -
$MnCO_3$[a]	Solid	7.79	$4.21 \cdot 10^{-2}$	$-.90 \cdot 10^{-5}$	0 - 500
$MnSO_4$[a]	Anhydrous	22.5	$1.5 \cdot 10^{-2}$		0 - 1,000
$MnCl_2$[a]	Solid	16.38	$5.0 \cdot 10^{-3}$		0 - 650
Do[a]	Liquid	24			650 -
Do[a]	Vapor	12	2.10^{-3}		650 -

a Estimated from low temperature data, etc.

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TABLE 62. - Summary of Standard Free Energies of Formation

Material	Reference state	Temperature, °K.	ΔF°
$Mn(\beta)$	$Mn(\alpha)$	298	+456
$Mn(\gamma)$	do	298	[1] -42
$Mn(l)$	do	298	[1] -3,533
$Mn(g)$	do	298	+48,913
Mn^{++}	$Mn(\alpha)$?	291	-52,450 ± 500
MnO	$Mn(\alpha)$, $1/2\ O_2$	298	-91,310 ± 700
$Mn(OH)_2$	$Mn(\alpha)$, O_2, H_2	291	-145,960 ± 1,000
Do	MnO, H_2O	291	+1,860 ± 1,000
Mn_3O_4	$3Mn(\alpha)$, $2O_2$	298	-319,820 ± 500
Mn_2O_3	$2Mn(\alpha)$, $3/2\ O_2$	298	-215,040 ± 3,000
MnO_2	$Mn(\alpha)$, O_2	298	-108,610 ± 1,000
MnS	$Mn(\alpha)$, S(rh)	298	-47,025 ± 500
$MnCO_3$	MnO, CO_2	298	-15,913 ± 300
Do	$Mn(\alpha)$, C(gr.), $3O_2$	298	-201,000 ± 1,000
$MnSO_4$	$Mn(\alpha)$, S(rh) $2O_2$	298	-226,935 ± 1,500
$MnCl_2$(g)	$MnCl_2$(l)	298	+31,972
$MnCl_2$(s)	$Mn(\alpha)$, Cl_2	298	-102,107 ± 500
$MnCl_2$(l)	$MnCl_2$(s)	298	+3,603 ± 500
Do	$Mn(\alpha)$, Cl_2	298	-98,504 ± 1,000
Mn_3C_4(in sol.)	3Mn(l), 4C(s)	298	+3,705
Mn_3C_4(solid sol.)	3Mn(s), 4C	298	-32,310
Mn_3N_2(amorph. solid sol.)	3Mn(s), N_2	298	-7,270
Mn_3N_2(mixed cryst.)	3Mn(s), N_2	298	-25,315
Mn_3N_2(dissolved)	3Mn(l), N_2	298	-35,160

[1] These values should obviously be positive, since a negative value would seem to indicate the product stable with respect to alpha manganese at 298°K. The difficulty is due to the long extrapolation of specific heat values, beyond the range where such values are truly valid. These figures are to be regarded simply as formal coefficients in the standard free energy equation, the use of which will make calculated values, in the range where the specific heat values are valid, fit the known experimental facts.

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TABLE 63. - Summary of Free-Energy Equations

$(\triangle F^{\circ}_T = \triangle H_0 + A\,T\,\ln T + BT^2 + CT^3 + I\,T)$

Product	Reference State or Reactant	$\triangle H_0$	A	B	C	I
$Mn(\beta)$	$Mn(\alpha)$	-1,102	-5.22	$+3.69 \cdot 10^{-3}$	- - -	+33.52
$Mn(\gamma)$	$Mn(\beta)$	-1,073	-1.0	- - -	- - -	+ 7.99
Mn(l)	$Mn(\gamma)$	-5,516	-1.30	- - -	- - -	+11.01
Mn(g)	Mn(l)	+65,930	+6.33	- - -	- - -	-77.92
$Mn(\gamma)$	$Mn(\alpha)$	-2,175	-6.22	$+3.69 \cdot 10^{-3}$	- - -	+41.46
Mn(l)	$Mn(\alpha)$	-7,691	-7.55	$+3.69 \cdot 10^{-3}$	- - -	+52.47
Mn(g)	$Mn(\alpha)$	+58,239	-1.22	$+3.69 \cdot 10^{-3}$	- - -	-25.45
MnO	$Mn(\alpha)$, $1/2\ O_2$	-96,700	- .40	$-1.25 \cdot 10^{-3}$	$+0.60 \cdot 10^{-6}$	+20.68
Mn_2O_3	$2Mn(\alpha)$, $3/2\ O_2$	-234,370	+6.98	$-1.83 \cdot 10^{-2}$	$+ .423 \cdot 10^{-5}$	+30.15
Mn_3O_4	$3Mn(\alpha)$, $2O_2$	-344,627	+5.09	$-1.485 \cdot 10^{-2}$	$+ .332 \cdot 10^{-5}$	+58.35
MnO_2	$Mn(\alpha)$, O_2	-120,230	+8.36	$-1.94 \cdot 10^{-2}$	$+ .495 \cdot 10^{-5}$	-3.31
$2Mn_2O_3$	$4MnO_2, O_2$	+12,296	-19.48	$+4.22 \cdot 10^{-2}$	$-1.123 \cdot 10^{-5}$	+72.80
$4Mn_3O_4$	$6Mn_2O_3, O_2$	+29,027	-21.52	$+5.09 \cdot 10^{-2}$	$+1.177 \cdot 10^{-5}$	+45.67
MnS	$Mn(\alpha)$, S(rh)	-46,313	-2.31	$+2.76 \cdot 10^{-3}$	$+ .403 \cdot 10^{-6}$	+9.90
$MnCO_3$	MnO, CO_2	-27,245	+7.34	$-1.32 \cdot 10^{-2}$	$+ .76 \cdot 10^{-6}$	+ .10
$MnCl_2(g)$	$MnCl_2(l)$	+46,950	+12.0	$-2 \cdot 10^{-3}$	- - -	-118.27
$MnCl_2(s), H_2S$	MnS, 2HCl	-27,481	+ .15	$- .451 \cdot 10^{-3}$	$- .36 \cdot 10^{-6}$	+32.64
$MnCl_2(l)$	$MnCl_2(s)$	+ 2,206	-7.62	$+2.5 \cdot 10^{-3}$	- - -	+47.30
Mn_3C_4(liq. sol.)	3Mn(l), 4C	+ 3,090	- -	- - -	- - -	+ 2.062
Mn_3C_4(solid sol.)	3Mn(s), 4C	-52,780	- -	- - -	- - -	+67.00
Mn_3N_2(amorph. solid s.)	3Mn(s), N_2	-10,300	- -	- - -	- - -	+10.16
Mn_3N_2(mix.cryst.)	3Mn(s), N_2	-33,460	- -	- - -	- - -	+27.32
Mn_3N_2(dissolved)	3Mn(l), N_2	-45,800	- -	- - -	- - -	+35.70

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TABLE 64. - Summary of Entropy and Heat of Formation Values

Material	S_{298}	ΔH_{298}
Mn (α)	7.3 ± 0.5	0
MnO	14.4 ± 0.6	-96,500 ± 650
$Mn(OH)_2$	1/ 23.9 ± 1.5	-165,000 ± 2,000
Mn_2O_3	1/ 21.1 ± 2.0	-235,050 ± 5,000
Mn_3O_4	35.5 ± 0.7	-345,000 ± 1,000
MnO_2	13.9 ± 0.4	-121,260 ± 2,000
MnS	18.7 ± 0.3	-45,890 ± 300
$MnCO_3$	20.5 ± 0.4	-219,100 ± 800
$MnSO_4$	1/ 33.1 ± 3.0	-250,735 ± 1,500
$MnCl_2(g)$	- -	2/ +43,550 ± 500
$MnCl_2(s)$	1/ 25.1 ± 2.0	-112,600 ± 1,000
$MnCl_2(l)$	- -	-108,344 ± 1,500

1/ Estimates, not directly determined.

2/ From liquid.

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